(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 518 238 A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 92109588.1

(22) Date of filing: 05.06.92

(51) Int. Cl.5: C07D 487/04

(30) Priority: 07.06.91 JP 162324/91
27.11.91 JP 311212/91
27.11.91 JP 335861/91
21.02.92 JP 69980/92

(43) Date of publication of application:
16.12.92 Bulletin 92/51

(84) Designated Contracting States:
CH DE FR GB LI NL

(71) Applicant: FUJI PHOTO FILM CO., LTD.
210 Nakanuma Minami Ashigara-shi
Kanagawa(JP)

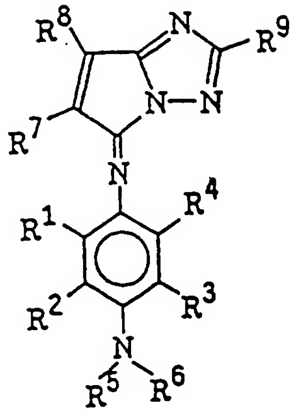
(72) Inventor: Suzuki, Makoto, c/o Fuji Photo Film Co., Ltd.
210, Nakanuma
Minami, Ashigara-shi, Kanagawa(JP)
Inventor: Mikoshiba, Hisashi, c/o Fuji Photo Film Co., Ltd.
210, Nakanuma
Minami, Ashigara-shi, Kanagawa(JP)
Inventor: Takahashi, Osamu, c/o Fuji Photo Film Co., Ltd.
210, Nakanuma
Minami, Ashigara-shi, Kanagawa(JP)
Inventor: Shimada, Yasuhiro, c/o Fuji Photo Film Co., Ltd.
210, Nakanuma
Minami, Ashigara-shi, Kanagawa(JP)
Inventor: Matsuoka, Koushin, c/o Fuji Photo Film Co., Ltd.
210, Nakanuma
Minami, Ashigara-shi, Kanagawa(JP)
Inventor: Yamazaki, Shigeru, c/o Fuji Photo Film Co., Ltd.
210, Nakanuma
Minami, Ashigara-shi, Kanagawa(JP)
Inventor: Yamakawa, Kazuyoshi, c/o Fuji Photo Film Co., Ltd.
210, Nakanuma
Minami, Ashigara-shi, Kanagawa(JP)
Inventor: Sato, Kozo, c/o Fuji Photo Film Co., Ltd.
210, Nakanuma
Minami, Ashigara-shi, Kanagawa(JP)

(74) Representative: Patentanwälte Grünecker, Kinkeldey, Stockmair & Partner
Maximilianstrasse 58
W-8000 München 22(DE)

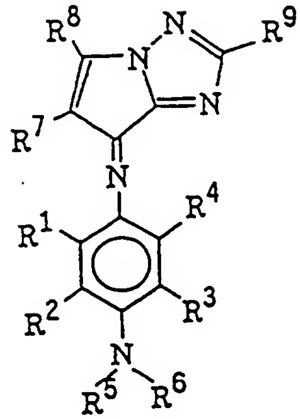
(54) Pyrrolotriazole derivative.

(57) A novel pyrrolotriazole derivative is disclosed, represented by any one of formulae (I), (II), or (III):

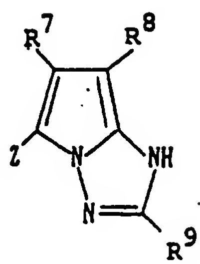
EP 0 518 238 A1



(I)



(II)



(III)

wherein:

R^1, R^2, R^3 and R^4 each independently represents a hydrogen atom or a nonmetallic atomic group;

R^5 and R^6 each independently represents a hydrogen atom, alkyl group, an aryl group, or a heterocyclic group;

R^7 represents an electrophilic group having a Hammett's substituent constant σ_p of 0.15 or more;

R^8 and R^9 each independently represents a hydrogen atom or a nonmetallic atomic group;

the sum of Hammett's substituent constant σ_p of R^7 and R^8 is 0.65 or more;

R^1 and R^2, and/or R^2 and R^5, and/or R^5 and R^6, and/or R^6 and R^3, and/or R^3 and R^4 may be connected to each other to form a cyclic structure;

R^7 and R^8 may be connected to each other to form a cyclic structure; and

Z represents a hydrogen atom, a halogen atom, an arylthio group, a heterocyclic thio group, an arylsulfinyl group, or a nitroso group.

The present invention relates to a novel pyrrolotriazole derivative

1H-Pyrrolo-[1,2-b][1,2,4]triazole derivaties are useful as synthesis intermediates of physiologically active substances such as pharmaceutical preparations and pesticides. These derivatives are also known as coupler nuclei and dyes which exhibit reduced secondary absorption in the field of photographic chemistry (proceedings of the 60th Annual Conference of The Society of Photographic Science and Technology of Japan). However, 1H-pyrrolo-[1,2-b][1,2,4]triazole dyes which have heretofore been known exhibit a maximum absorption wavelength of lower than 560 nm. No 1H-pyrrolo-[1,2-b][1,2,4]triazole dyes which exhibit a maximum absorption wavelength of higher than 600 nm have been known.

In recent years, 1H-pyrrolo-[1,2-b][1,2,4]triazole dyes which exhibit a maximum absorption wavelength of higher than 560 nm, particularly 600 nm have been desired. In other words, dyes containing a 1H-pyrrolo-[1,2-b][1,2,4]triazole nucleus which exhibit reduced secondary absorption and a primary absorption wavelength of higher than 600 nm have been keenly desired.

Furthermore, in recent years, new color image formation methods such as color electrophotography, ink jet printing process and heat-sensitive transfer process have been proposed. On the other hand, with the development of electronic imaging technique, the demand for solid state image pick-up tube and filter for color liquid crystal television set has increased. Thus, azomethine dyes have been applied and reviewed in color photography as well as various systems or merchandise.

As cyan azomethine dyes in these applications there have been known phenol and naphthol azomethine dyes. Furthermore, imidazole azomethine dyes and hydroxypyridine azomethine dyes have been known.

Moreover, pyrazoloazole azomethine dyes, pyrazolopyrimidin-5-one azomethine dyes, pyrazoloquinazolone azomethine dyes, pyrazolotriazine azomethine dyes and cyan azomethine dyes have been known.

However, these known azomethine dyes have various disadvantages. For example, phenol and naphthol azomethine dyes exhibit too broad an absorption to serve as dyes for filter. Further, imidazole azomethine dyes are disadvantageous in that they exhibit a low fastness to light. Moreover, pyrazolopyrimidin-5-one azomethine dyes, pyrazoloquinazolone azomethine dyes and pyrazolotriazine azomethine dyes exhibit too broad an absorption. Further, pyrazolotriazole azomethine dyes exhibit a low fastness to light. Moreover, hydroxypyridine azomethine dyes can hardly be synthesized and exhibit a low fastness to light.

Thus, among known azomethine dyes, there are no dyes which exhibit an absorption waveform suitable for cyan color and a high fastness to light and heat. Therefore, the development of azomethine dyes which exhibit a sharp absorption and a high fastness has been keenly desirerd.

In order to overcome these difficulties, the inventors made a study on novel azomethine dyes. As a result, it was found that pyrrolotriazole azomethine dyes having a specific structure which has never been known exhibit a sharp absorption and a high fastness to light. Thus, the present invention was worked out.

Pyrrolotriazole couplers are disclosed in JP-A-62-279340 and 62-278552 (the term "JP-A" as used herein means an "unexamined published Japanese patent application").

Even if the foregoing techniques are known, the present invention is by no means limited thereby.

The above mentioned known couplers are considered to undergo color development to produce azomethine dyes. According to the above cited references, the color of the dyes thus produced are magenta.

The inventors' study showed that pyrrolotriazole azomethine dyes represented by formulae (I) and (II) given later exhibit a cyan color when its coupler portion is such that Hammett's substituent constant σ_p of R^7 is 0.15 or more and the sum of Hammett's substituent constant σ_p of R^7 and R^8 is 0.65 or more.

In the above cited references, there is no reference to couplers which will give an azomethine dye that exhibits a cyan color. There is neither reference that gives an expectation of a specific structure that exhibits a cyan color.

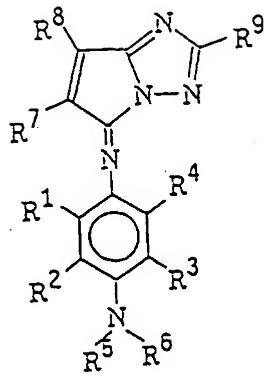
In other words, it was disclosed for the first time by the inventors, who made a study on the relationship between the substituents R^7 and R^8 and the absorption characteristics of dye, that novel pyrrolotriazole azomethine dyes of the present invention exhibit an excellent cyan color. It is extremely difficult to expect this fact from the above cited references.

It is therefore an object of the present invention to provide a novel pyrrolotriazole derivative.

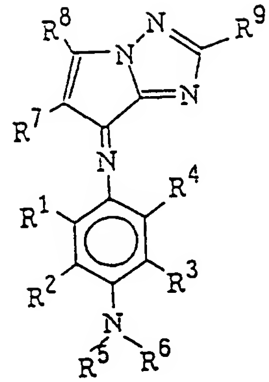
It is another object of the present invention to provide a pyrrolotriazole azomethine dye which exhibits a sharp absorption and a high fastness to heat and light.

These and other objects of the present invention will become more apparent from the following detailed description and examples.

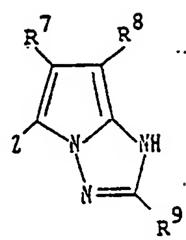
These objects of the present invention are accomplished with pyrrolotriazole derivatives represented by formulae (I) to (III):



(I)



(II)



(III)

In the above formulae (I) to (III), R^1, R^2, R^3 and R^4 each independently represents a hydrogen atom or nonmetallic atomic group.

R^5 and R^6 each independently represents a hydrogen atom, alkyl group, aryl group or heterocyclic group.

R^7 represents an electrophilic group having a Hammett's substituent constant σ_p of 0.15 or more.

R^8 and R^9 each independently represents a hydrogen atom or nonmetallic atomic group.

The sum of Hammett's substituent constant σ_p of R^7 and R^8 is 0.65 or more.

R^1 and R^2, and/or R^2 and R^5, and/or R^5 and R^6, and/or R^6 and R^3, and/or R^3 and R^4 may be connected to each other to form a cyclic structure.

R^7 and R^8 may be connected to each other to form a cyclic structure.

Z represents a hydrogen atom, halogen atom, arylthio group, heterocyclic thio group, arylsulfinyl group or nitroso group.

Fig. 1 shows the absoption spectrum of ethyl acetate solution of exemplary Compound (I-2) and a comparative dye a.

Among the compounds represented by formulae (I) to (III), those represented by formulae (I) and (II) are useful as cyan dyes.

Further, the 1H-pyrrolo-[1,2-b][1,2,4]triazole derivatives represented by formula (III) are useful as synthesis intermediates of the compounds represented by formulae (I) and (II), or physiologically active substances such as pharmaceutical preparations and pesticides.

Formulae (I) to (III) will be further described hereinafter.

Hammett's substituent constant as used herein will be now briefly discussed. Hammett's rule is an empirical law which was proposed in 1935 by L. P. Hammett to give a quantative discussion of the effect of substituents on the reaction or equilibrium of benzene derivatives. This rule is now widely considered reasonable. Substituent constants determined by Hammett's rule include σ_p value and σ_m value which can be found in many general references, e.g., J.A. Dean, Lange's Handbook of Chemistry, vol. 12, 1979 (McGraw-Hill), and Kagaku No Ryoiki (The Domain of Chemistry), extra edition, No. 122, pp. 96 - 103, 1979 (Nankodo). In the present invention, various substituents are limited or illustrated by Hammett's substituent constant σ_p. However, this doesn't mean that these substituents are limited to those having known σ_p values found in the above cited references. It goes without saying that even when these substituents exhibit σ_p values unknown in any reference, they are included in those having σ_p values that would be included in the range known in these references when measured according to Hammett's rule. The value of σ_p will be hereinafter defined in this manner.

R^1, R^2, R^3 and R^4 each independently represents a hydrogen atom or nonmetallic atomic group. Examples of the nometallic atomic group include halogen atom, alkyl group, aryl group, heterocyclic group, cyano group, hydroxyl group, nitro group, carboxyl group, sulfonic acid group, amino group (including substituted amino group), alkoxy group, aryloxy group, acylamino group, aminocarbonylamino group, sulfamoylamino group, alkylthio group, arylthio group, alkoxycarbonylamino group, sulfonylamino group, carbamoyl group, sulfamoyl group, sulfonyl group, alkoxycarbonyl group, heterocyclic oxy group, azo group, acyloxy group, carbamoyloxy group, silyloxy group, aryloxycarbonyl group, imido group, heterocyclic thio group, sulfinyl group, phosphoryl group, formyl group, acyl group, and azolyl group. Of these non-metallic atomic groups, those which can contain substituents may be substituted by substituents such as halogen atom, hydroxyl group, carboxyl group, sulfo group, cyano group, nitro group, amino group, alkyl group, alkenyl group, alkynyl group, aryl group, alkoxy group, aryloxy group, alkylthio group, arylthio group, alkylsulfonyl group, arylsulfonyl group, acyl group, acyloxy group, alkoxycarbonyl group, aryloxycarbonyl group, carbonamido group, sulfonamido group, carbamoyl group, sulfamoyl group, ureido group, alkoxycarbonylamino group, sulfamoylamino group, alkoxysulfonyl group, imido group and heterocyclic group (these substituents will be hereinafter referred to as "substituent group A").

Specific examples of R^1, R^2, R^3 and R^4 include hydrogen atom, alkyl group (preferably alkyl group having a total carbon atom number of from 1 to 30 (hereinafter expressed as "C_{1-30} alkyl group"), e.g., methyl, ethyl, propyl, butyl), alkoxy group (preferably C_{1-30} alkoxy group, e.g., methoxy, ethoxy, methoxyethoxy, isopropoxy), halogen atom (e.g., bromine, fluorine, chlorine), acylamino group (preferably C_{1-30} alkylcarbonylamino group, e.g., formylamino, acetylamino, propionylamino, cyanoacetylamino, or preferably C_{7-30} arylcarbonylamino group, e.g., benzoylamino, p-toluylamino, pentafluorobenzoylamino, m-methoxybenzoylamino), alkoxycarbonyl group (preferably C_{2-30} alkoxycarbonyl group, e.g., methoxycarbonyl, ethoxycarbonyl), cyano group, sulfonylamino group (preferably C_{1-30} sulfonylamino group, e.g., methanesulfonylamino, ethanesulfonylamino, N-methylmethanesulfonylamino), carbamoyl group (preferably C_{2-30} carbamoyl group, e.g., methylcarbamoyl, dimethylcarbamoyl, butylcarbamoyl, isopropylcarbamoyl, t-butylcarbamoyl, cyclopentylcarbamoyl, cyclohexylcarbamoyl, methoxyethylcarbamoyl, chloroethylcarbamoyl, cyanoethylcarbamoyl, ethylcyanoethylcarbamoyl, benzylcarbamoyl, ethoxycarbonylmethylcarbamoyl, furfurylcarbamoyl, tetrahydrofurfurylcarbamoyl, phenoxymethylcarbamoyl, allylcarbamoyl, crotylcarbamoyl, prenylcarbamoyl, 2,3-dimethyl-2-butenylcarbamoyl, homoallylcarbamoyl, homocrotylcarbamoyl, homoprenylcarbamoyl, preferably C_{7-30} arylcarbamoyl group, e.g., phenylcarbamoyl, p-toluylcarbamoyl, m-methoxyphenylcarbamoyl, 4,5-dichlorophenylcarbamoyl, p-cyanophenylcarbamoyl, p-acetylaminophenylcarbamoyl, p-methoxycarbonylphenylcarbamoyl, m-trifluoromethylphenylcarbamoyl, o-fluorophenylcarbamoyl, 1-naphthylcarbamoyl, or preferably C_{4-30} heterylcarbamoyl group, e.g., 2-pyridylcarbamoyl, 3-pyridylcarbamoyl, 4-pyridylcarbamoyl, 2-thiazolylcarbamoyl, 2-benzthiazolylcarbamoyl, 2-benzimidazolylcarbamoyl, 2-(4-methylphenyl)-1,3,4-thiazolylcarbamoyl), sulfamoyl group (preferably C_{0-30} sulfamoyl group, e.g., methylsulfamoyl, dimethylsulfamoyl), aminocarbonylamino group (preferably C_{1-30} aminocarbonylamino group, e.g., methylaminocarbonylamino, dimethylaminocarbonylamino), alkoxycarbonylamino group (preferably C_{2-30} alkoxycarbonylamino group, e.g., methoxycarbonylamino, ethoxycarbonylamino), hydroxyl group, carboxyl group (including salts thereof), sulfonic acid group (including salts thereof), amino group (preferably C_{0-30} amino group, e.g., amino, methylamino, dimethylamino, anilino), aryl group (preferably C_{6-30} aryl group, e.g., phenyl, m-acetylphenyl, p-methoxyphenyl), heterocyclic group (preferably C_{3-30} heterocyclic group, e.g., 2-pyridyl, 2-furyl, 2-tetrahydrofuryl), nitro group, aryloxy group (preferably C_{6-30} aryloxy group, e.g., phenoxy, p-methoxyphenoxy, o-chlorophenoxy), sulfamoylamino group (preferably C_{0-30} sulfamoylamino group, e.g., methylsulfamoyl, dimethylsulfamoyl), alkylthio group (preferably C_{1-30} alkylthio group, e.g., methylthio, ethylthio), arylthio group (preferably C_{6-30} arylthio group, e.g., phenylthio, p-methoxyphenylthio, o-chlorophenylthio), sulfonyl group (preferably C_{1-30} sulfonyl group, e.g.,

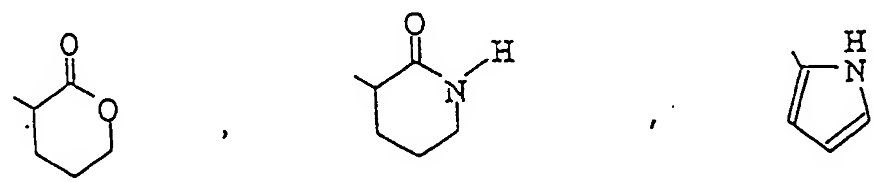
methanesulfonyl, p-toluenesulfonyl), formyl group, acyl group (preferably C_{1-30} acyl group, e.g., acetyl, benzoyl, p-toluyl), heterocyclic oxy group (preferably C_{3-30} heterocyclic oxy group), azo group (preferably C_{3-30} azo group, e.g., p-nitrophenylazo), acyloxy group (preferably C_{1-30} acyloxy group, e.g., acetyloxy, benzoyloxy), carbamoyloxy group (preferably C_{1-30} carbamoyloxy group, e.g., methylcarbamoyloxy), silyloxy group (preferably C_{3-30} silyloxy group, e.g., trimethylsilyloxy), aryloxycarbonyl group (preferably C_{7-30} aryloxycarbonyl group, e.g., phenoxycarbonyl), imido group (preferably C_{4-30} imido group, e.g., phthalimido), heterocyclic thio group (preferably C_{3-30} heterocyclic thio group), sulfinyl group (preferably C_{1-30} sulfinyl group, e.g., diethylaminosulfinyl), phsophoryl group (preferably C_{0-30} phosphoryl group, e.g., diaminophosphoryl), and azolyl group (preferably C_{2-30} azolyl group, e.g., 2-pyrazolyl).

Preferred among the groups represented by R^2, R^3 and R^4 is hydrogen atom.

Preferred among the groups represented by R^1 are hydrogen atom, C_{1-30} alkyl group, C_{1-30} alkoxy group, halogen atom (e.g., fluorine, chlorine, bromine), C_{1-30} acylamino group, C_{1-30} sulfonylamino group, C_{1-30} aminocarbonylamino group, and C_{2-30} alkoxycarbonylamino group. Particularly preferred among these groups are hydrogen atom, alkyl group, and acylamino group.

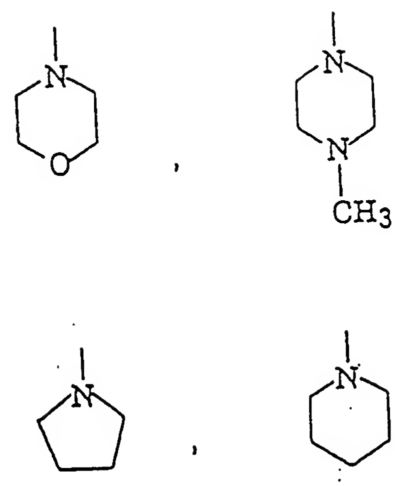
R^5 and R^6 each independently represents a hydrogen atom, alkyl group, aryl group, or heterocyclic group. The alkyl group, aryl group, and heterocyclic group may be substitued by substituents such as substituent group A.

Specific examples of R^5 and R^6 include a hydrogen atom, alkyl group (preferably C_{1-30} alkyl group, e.g., methyl, ethyl, propyl, isopropyl, butyl, octyl, 2-aminoethyl, 2-carbamoylethyl, 2-carboxyethyl, 4-sulfobutyl, 3-(4-methoxyphenoxy)propyl, 2-methanesulfonamidoethyl, 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-methoxyethyl, 3-methoxypropyl, ethoxyethyl, 2-phenylethyl, 2-cyanoethyl, cyanomethyl, 2-chloroethyl, 3-bromopropyl, 2-methoxycarbonylethyl, 3-ethoxycarbonylpropyl, 2-(N-methylaminocarbonyl)-ethyl, 3-(N,N-dimethylaminocarbonyl)propyl, 2-acetylaminoethyl, 3-(ethylcarbonylamino)propyl, allyl homoallyl, prenyl, n-dodecyl, 2-acetyloxyethyl), aryl group (preferably C_{6-30} aryl group, e.g., phenyl, p-tolyl, p-methoxyphenyl, 2,4-dichlorophenyl, p-nitrophenyl, 2,4-dicyanophenyl, 2-naphthyl) or heterocyclic group (including those containing substituents, preferably C_{3-30} heterocyclic group such as those represented by the following formulae).

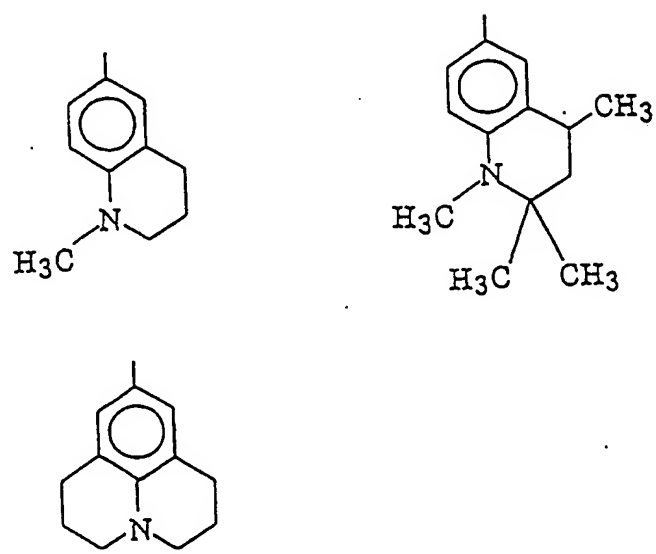


Preferred among the groups represented by R^5 and R^6 is a C_{1-30} alkyl group which may be substituted (e.g., methyl, ethyl, propyl, 2-cyanoethyl, 2-acetyloxyethyl, 2-ethoxycarbonylethyl, 2-methoxyethyl, 2-methanesulfonamidoethyl, 2-hydroxyethyl, 3-hydroxypropyl, allyl, homoallyl, prenyl).

Examples of the ring which R^5 and R^6 may be connected to each other to form include those represented by the following formulae:



Preferred examples of the ring which R^2 and R^5, and/or R^3 and R^6, may be connected to each other to form include those represented by the following formulae:



R^7 represents an electrophilic group having a Hammett's substituent constant σ_p of 0.15 or more.

Examples of R^7 include formyl group, acyl group, acyloxy group, carbamoyl group, alkoxycarbonyl group, aryloxycarbonyl group, cyano group, carboxyl group, nitro group, dialkylphosphono group, diarylphosphono group, diarylphosphinyl group, alkylsulfinyl group, arylsulfinyl group, alkylsulfonyl group, arylsulfonyl group, arylthio group, sulfonyloxy group, acylthio group, sulfamoyl group, isocyanato group, thiocyanato group, thiocarbonyl group, alkyl group substituted by at least two halogen atoms, alkoxy group substituted by at least two halogen atoms, aryloxy group substituted by at least two halogen atoms, alkylamino group substituted by at least two halogen atoms, alkylthio group substituted by at least two halogen atoms, aryl group substituted by other electrophilic groups having a Hammett's substituent constant σ_p of 0.15 or more, heterocyclic group, chlorine atom, bromine atom, and selenocyanato group. Of these groups, those which can contain substituents may be substituted by substituents such substituent group A.

Specific examples of R^7 include acyl group (e.g., acetyl, 3-phenylpropanoyl, benzoyl, 4-dodecyloxybenzoyl), acyloxy group (e.g., acetoxy), carbamoyl group (e.g., N-ethylcarbamoyl, N,N-dibutylcarbamoyl, N-(2-

dodecyloxyethyl)carbamoyl, N-methyl-N-dodecylcarbamoyl, N-[3-(2,4-di-t-amylphenoxy)propyl]carbamoyl), alkoxycarbonyl group (preferably straight-chain, branched or cyclic alkoxycarbonyl group, e.g., methoxycarbonyl, ethoxycarbonyl, isopropoxycarbonyl, isobutoxycarbonyl, n-octyloxycarbonyl, n-decyloxycarbonyl, n-dodecyloxycarbonyl, n-hexadecyloxycarbonyl, 2-ethylhexyloxycarbonyl, 3,5,5-trimethylhexyloxycarbonyl, 2-ethyl-4-methylpentyloxycarbonyl, 2-hexyldecyloxycarbonyl, 2-heptylundecyloxycarbonyl, 2-octyldodecyloxycarbonyl, 2,4,6-trimethylheptyloxycarbonyl, 2,4,6,8-tetramethylnonyloxycarbonyl, benzyloxycarbonyl, 2-phenethyloxycarbonyl, 3-(t-octylphenoxy)propoxycarbonyl,3-(2,4-di-t-pentylphenoxy)propoxycarbonyl, 2-(4-biphenyloxy)ethoxycarbonyl, 3-dodecyloxypropoxycarbonyl, 2-dodecylthioethoxycarbonyl, 9,10-epoxyoctadecyloxycarbonyl, dodecyloxycarbonylmethoxycarbonyl, 2-(2-naphthyloxy)ethoxycarbonyl, 7,7-dimethyl-2-(3',3'-dimethylbutyl)-5-methyloctyloxycarbonyl, 2-methyl-cyclohexyloxycarbonyl, 2-hexyl-cyclohexyloxycarbonyl), aryloxycarbonyl group (e g., phenoxycarbonyl), cyano group, carboxyl group, nitro group, dialkylphosphono group (e g., dimethylphosphono), diarylphosphono group (e.g., diphenylphosphono), diarylphosphinyl group (e.g., diphenylphosphinyl), alkylsulfinyl group (e.g., 3-phenoxypropylsulfinyl), arylsulfinyl group (e.g., 3-pentadecylphenylsulfinyl), alkylsulfonyl group (e.g., methanesulfonyl, octanesulfonyl), arylsulfonyl group (e.g., benzenesulfonyl, toluenesulfonyl), alkylthio group (e.g., methylthio, octylthio, tetradecylthio, 2-phenoxyethylthio, 3-phenoxypropylthio, 3-(4-t-butylphenoxy)propylthio), arylthio group (e.g., phenylthio, 2-butoxy-5-t-octylphenylthio, 3-pentadecylphenylthio, 2-carboxyphenylthio, 4-tetradecanamidophenylthio), sulfonyloxy group (e.g., methanesulfonyloxy, toluenesulfonyloxy), acylthio group (e.g., acetylthio, benzoylthio), sulfamoyl group (e.g., N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-(2-dodecyloxyethyl)-sulfamoyl, N-ethyl-N-dodecylsulfamoyl, N,N-diethylsulfamoyl), isocyanato group, thiocyanato group, thiocarbonyl group (e.g., methylthiocarbonyl, phenylthiocarbonyl), alkyl group substituted by at least two halogen atoms (e.g., trifluoromethane, heptafluoropropane), alkoxy group substituted by at least two halogen atoms (e.g., trifluoromethyloxy), aryloxy group substituted by at least two halogen atoms (e.g., pentafluorophenyloxy), alkylamino group substituted by at least two halogen atoms (e.g., N,N-di-(trifluoromethyl)amino), alkylthio group substituted by at least two halogen atoms (e.g., difluoromethylthio, 1,1,2,2-tetrafluoroethylthio), aryl group substituted by two or more electrophilic groups having a Hammett's substituent constant σ_p of 0.15 or more (e.g., 2,4-dinitrophenyl, 2,4,6-trichlorophenyl, pentachlorophenyl), heterocyclic group (e.g., 2-benzoxazolyl, 2-benzothiazolyl, 1-phenyl-2-benzimidazolyl, 5-chloro-1-tetrazolyl, 1-pyrrolyl), chlorine atom, bromine atom, and selenocyanato group.

Among these substituents, those which can further contain substituents may further contain halogen atoms or substituents connected via carbon atom, oxygen atom, nitrogen atom or sulfur atom thereto.

Examples of σ values of typical electrophilic groups having a Hammett's substituent constant σ_p of 0.15 or more include 0.66 for cyano group, 0.45 for carboxyl group, 0.78 for nitro group, 0.54 for trifluoromethyl group, 0.50 for acetyl group, 0.92 for trifluoromethanesulfonyl group, 0.72 for methanesulfonyl group, 0.70 for benzenesulfonyl group, 0.49 for methanesulfinyl group, 0.36 for carbamoyl group, 0.45 for methoxycarbonyl group, 0.44 for phenoxycarbonyl group, 0.37 for pyrazolyl group, 0.36 for methanesulfonyloxy group, 0.33 for benzenesulfonyloxy group, 0.60 for dimethoxyphosphoryl group, 0.57 for sulfamoyl group, 0.42 for formyl group, 0.31 for acetoxy group, 0.18 for phenylthio group, 0.44 for acetylthio group, 0.23 for chlorine atom, 0.23 for bromine atom, 0.29 for tribromomethyl group, 0.33 for trifluoromethyl group, 0.54 for trifluoromethyl group, 0.41 for pentafluorophenyl group, 0.35 for trifluoroalkoxy group, 0.53 for N,N-trifluoromethanamino group, and 0.30 for 2,4,6-trinitrophenyl group.

Preferred among the groups represented by R^7 are formyl group, acyl group, acyloxy group, carbamoyl group, alkoxycarbonyl group, aryloxycarbonyl group, cyano group, nitro group, alkylsulfinyl group, arylsulfinyl group, alkylsulfonyl group, arylsulfonyl group, alkylsulfonyl group, sulfamoyl group, halogenated alkyl group, halogenated alkyloxy group, halogenated alkylthio group, halogenated aryloxy group, aryl group substituted by two or more electrophilic groups having a Hammett's substituent constant σ_p of 0.15 or more, and heterocyclic group.

Further preferred among these groups are formyl group, carbamoyl group, alkoxycarbonyl group, aryloxycarbonyl group, and cyano group. Particularly preferred among these groups are cyano group, alkoxycarbonyl group, and aryloxycarbonyl group.

That is, R^7 is preferably a cyano group or -COR wherein R is preferably a hydrogen atom, C_{0-36} amino group, C_{1-36}, preferably C_{1-24} straight-chain, branched or cyclic alkoxy group, or C_{6-36}, preferably C_{6-24} aryloxy group. These amino, alkoxy and aryloxy groups may be substituted by substituents such as substituent group A.

Alternatively, R^7 is preferably a cyano group or -COR wherein R is preferably an unsubstituted, alkyl-substituted, aryl-substituted or heterocyclic group-substituted amino group (these alkyl-substituted, aryl-substituted and heterocyclic group-substituted amino groups may be further substituted by the substituent group A; the alkyl in the alkyl-substituted amino group may be a straight-chain, branched or cyclic alkyl

group; examples of such alkyl-substituted amino groups include amino, ethylamino, n-dodecylamino, anilino, 2-chloroanilino, 2-naphthylamino, 2-pyridyl-2-amino), straight-chain, branched or cyclic unsubstituted alkoxy group or alkoxy group containing substituents such as alkoxy group, alkylthio group, aryloxy group, arylthio group, alkylsulfonyl group, arylsulfonyl group, aryl group, alkoxycarbonyl group, epoxy group, cyano group and halogen atom (e.g., methoxy, ethoxy, isopropoxy, isobutoxy, n-octyloxy, n-decyloxy, n-dodecyloxy, n-hexadecyloxy, 2-ethylhexyloxy, 3,5,5-trimethylhexyloxy, 2-ethyl-4-methylpentyloxy, 2-hexyldecyloxy, 2-heptylundecyloxy, 2-octyldodecyloxy, 2,4,6-trimethylheptyloxy, 2,4,6,8-tetramethylnonyloxy, benzyloxy, 2-phenethyloxy, 3-(t-octylphenoxy)propoxy, 3-(2,4-di-t-pentyphenoxy)propoxy, 2-(4-biphenyloxy)ethoxy, 3-dodecyloxypropoxy, 2-dodecylthioethoxy, 9,10-epoxyoctadecyloxy, dodecyloxycarbonylmethoxy, 2-(2-naphthyloxy)ethoxy, 7,7-dimethyl-2-(3',3'-dimethylbutyl)-5-methyloctyloxy, 2-methyl-cyclohexyloxy, 2-hexylcyclohexyloxy), unsubstituted aryloxy group or aryloxy group containing substituents (substituent group A) (e.g., phenoxy, 2-t-amylphenoxy, 4-dodecyloxyphenoxy).

R^8 and R^9 each independently represents a hydrogen atom or nonmetallic atomic group. In particular, R^8 and R^9 each independently represents a hydrogen atom, aryl group, heterocyclic group, alkyl group, cyano group, carboxyl group, formyl group, acyl group, carbamoyl group, alkoxycarbonyl group, aryloxycarbonyl group, acylamino group, alkoxycarbonylamino group, aryloxycarbonylamino group, sulfonylamino group, aminocarbonylamino group, sulfamoylamino group, amino group (including anilino group), alkoxy group, aryloxy group, silyloxy group, heteryloxy group, alkylthio group, arylthio group, heterylthio group, halogen atom, hydroxyl group, nitro group, sulfamoyl group, sulfonyl group, azo group, acyloxy group, carbamoyloxy group, imido group, sulfinyl group, phosphoryl group or azolyl group. Of these nonmetallic atomic groups, those which can contain substituents may be substituted by substituents such as substituent group A.

Specific examples of R^8 and R^9 include hydrogen atom, aryl group (preferably C_{6-30} aryl group, e.g., phenyl, m-acetylaminophenyl, p-methoxyphenyl), alkyl group (preferably C_{1-30} alkyl group, e.g., methyl, ethyl, isopropyl, t-butyl, n-octyl, n-dodecyl), cyano group, carboxyl group, acyl group (preferably C_{1-30} acyl group, e.g., acetyl, pivaloyl, benzoyl, furoil, 2-pyridylcarbonyl), carbamoyl group (preferably C_{1-30} carbamoyl group, e.g., methylcarbamoyl, ethylcarbamoyl, dimethylcarbamoyl, n-octylcarbamoyl), alkoxycarbonyl group (preferably C_{1-30} alkoxycarbonyl group, e.g., methoxycarbonyl, ethoxycarbonyl, isopropoxycarbonyl), aryloxycarbonyl group (preferably C_{7-30} aryl group, e.g., phenoxycarbonyl, p-methoxyphenoxycarbonyl, m-chlorophenoxycarbonyl, o-methoxyphenoxycarbonyl), acylamino group (preferably C_{1-30} alkylcarbonylamino group, e.g., formylamino, acetylamino, propionylamino, cyanoacetylamino, C_{7-30} arylcarbonylamino group, e.g., benzoylamino, p-toluylamino, pentafluorobenzoylamino, m-methoxybenzoylamino, or C_{4-30} heterylcarbonylamino group, e.g., 2-pyridylcarbonylamino, 3-pyridylcarbonylamino, furoylamino), alkoxycarbonylamino group (preferably C_{2-30} alkoxycarbonylamino group, e.g., methoxycarbonylamino, ethoxycarbonylamino, methoxyethoxycarbonylamino), aryloxycarbonylamino group (preferably C_{7-30} aryloxycarbonylamino group, e.g., phenoxycarbonylamino, p-methoxyphenoxycarbonylamino, p-methylphenoxycarbonylamino, m-chlorophenoxycarbonylamino, o-chlorophenoxycarbonylamino), sulfonylamino group (preferably C_{1-30} sulfonylamino group, e.g., methanesulfonylamino, benzenesulfonylamino, toluenesulfonylamino), aminocarbonylamino group (preferably C_{1-30} aminocarbonylamino group, e.g., methylaminocarbonylamino, ethylaminocarbonylamino, anilinocarbonylamino, dimethylaminocarbonylamino), sulfamoylamino group (preferably C_{1-30} sulfamoylamino group, e.g., methylaminosulfonylamino, ethylaminosulfonylamino, anilinosulfonylamino), amino group (including anilino group, preferably C_{0-30} amino group, e.g., amino, methylamino, dimethylamino, ethylamino, diethylamino, n-butylamino, anilino), alkoxy group (preferably C_{1-30} alkoxy group, e.g., methoxy, ethoxy, isopropoxy, n-butoxy, methoxyethoxy, n-dodecyloxy), aryloxy group (preferably C_{6-30} aryloxy group, e.g., phenoxy, m-chlorophenoxy, p-methoxyphenoxy, o-methoxyphenoxy), silyloxy group (preferably C_{3-30} silyloxy group, e.g., trimethylsilyloxy, t-butyldimethylsilyloxy, cetyldimethylsilyloxy, phenyldimethylsilyloxy), heteryloxy group (preferably C_{3-30} heteryloxy group, e.g., tetrahydropyranyloxy, 3-pyridyloxy, 2-(1,3-benzimidazolyl)oxy), alkylthio group (preferably C_{1-30} alkylthio group, e.g., methylthio, ethylthio, n-butylthio, t-butylthio), arylthio group (preferably C_{6-30} arylthio group, e.g., phenylthio), heterylthio group (preferably C_{3-30} heterylthio group, e.g., 2-pyridylthio, 2-(1,3-benzoxazolyl)thio, 1-hexadecyl-1,2,3,4-tetrazolyl-5-thio, 1-(3-N-octadecylcarbamoyl)phenyl-1,2,3,4-tetrazolyl-5-thio), heterocyclic group (preferably C_{3-30} heterocyclic group, e.g., 2-benzoxazolyl, 2-benzothiazolyl, 1-phenyl-2-benzimidazolyl, 5-chloro-1-tetrazolyl, 1-pyrrolyl, 2-furanyl, 2-pyridyl, 3-pyridyl), halogen atom (e.g., fluorine, chlorine, bromine), hydroxyl group, nitro group, sulfamoyl group (preferably C_{0-30} sulfamoyl group, e.g., methylsulfamoyl, dimethylsulfamoyl), sulfonyl group (preferably C_{1-30} sulfonyl group, e.g., methanesulfonyl, benzenesulfonyl, toluenesulfonyl), azo group (preferably C_{3-30} azo group, e.g., p-nitrophenylazo), acyloxy group (preferably C_{1-30} acyloxy group, e.g., formyloxy, acetyloxy, benzoyloxy), carbamoyloxy group (preferably C_{1-30} aryl group, e.g., methylcar-

bamoyloxy, diethylcarbamoyloxy), imido group (preferably C_{4-30} imido group, e.g., succinimido, phthalimido), sulfinyl group (preferably C_{1-30} sulfinyl group, e.g., diethylaminosulfinyl), phosphoryl group (preferably C_{0-30} phosphoryl group, e.g., diaminophosphoryl), and azolyl group (preferably C_{2-30} azolyl group, e.g., 3-pyrazolyl).

Among these specific examples of R^8, σ_p values other than those described with reference to R^7 are 0.00 for hydrogen atom, -0.17 for methyl group, -0.15 for ethyl group, -0.01 for phenyl group, 0.00 for acetylamino group, 0.03 for methanesulfonamido group, -0.15 for carbonylamino group, etc.

R^8 preferably represents an electrophilic group having a Hammett's substituent constant σ_p of 0.15 or more, i.e., it is synonymous with R^7. Particularly preferred examples of R^8 include cyano group, formyl group, carbamoyl group, alkoxycarbonyl group, and aryloxycarbonyl group. That is, R^8 is preferably a cyano group or -COR wherein R is the same as defined above for R^7. More preferred among these groups are cyano group, alkoxycarbonyl group, and aryloxycarbonyl group. Particularly preferred among these groups are alkoxycarbonyl group and aryloxycarbonyl group.

In the present invention, the sum of σ_p values of R^7 and R^8 is 0.65 or more. Any combination of R^7 and R^8 is possible so far as R^7 has a σ_p value of 0.15 or more. Examples of such a combination will be set forth below, but the present invention should not be construed as being limited thereto.

R^7		R^8		Sum
CN	0.66	CN	0.66	1.32
CN	0.66	$COCH_3$	0.50	1.16
CN	0.66	CO_2CH_3	0.45	1.11
CN	0.66	$CONH_2$	0.36	1.02
$CONH_2$	0.36	$CONH_2$	0.36	0.72
$CONH_2$	0.36	CN	0.66	1.02
$CONH_2$	0.36	CO_2CH_3	0.50	0.86
$COCH_3$	0.50	CN	0.66	1.16
$COCH_3$	0.50	$COCH_3$	0.50	1.00
NO_2	0.78	C_6H_5	-0.01	0.77
CN	0.66	$CO_2C_6H_5$	0.44	1.10
$CO_2C_6H_5$	0.44	CHO	0.42	0.86
CN	0.66	$CONHCH_3$	0.36	1.02
CN	0.66	CF_3	0.54	1.20

Preferred examples of R^9 include aryl group, heterocyclic group, and alkyl group. Suitable among these groups is aryl group, preferably C_{6-36}, more preferably C_{6-30} aryl group. The aryl group is preferably an unsubstituted aryl group or an aryl group containing substituents (substituent group A) or which may be condensed (e.g., phenyl, 3-nitrophenyl, 4-nitrophenyl, 4-cyanophenyl, 3,4-dicyanophenyl, 3,4-dimethoxycarbonylphenyl,3-(2-octyloxy-5-t-octyl)phenylsulfonylaminophenyl, 3,5-dichlorophenyl, 4-[1-(2,4-di-t-amylphenoxy)propanoylamino]phenyl,4-(2-hexyldecyloxy)phenyl, 2-(2-hexyldecyloxy)phenyl, and 3-(2,4-di-t-amylphenoxyacetylamino)phenyl).

Preferred examples of substituents to be contained in the substituted aryl group include nitro group, halogen atom, cyano group, acylamino group, and sulfonamido group. Particularly preferred among these substituents is chlorine atom.

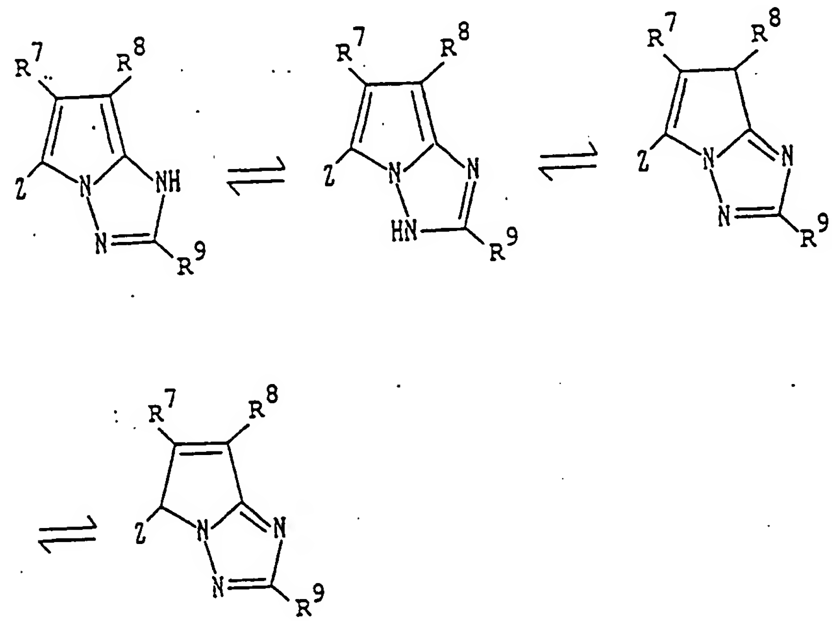
Z preferably represents a hydrogen atom, halogen atom, C_{6-36}, preferably C_{6-24} arylthio group, C_{1-36}, preferably C_{1-24} arylsulfinyl group, C_{1-36}, preferably C_{1-24} heterocyclic thio group, or nitroso group. These arylthio group, arylsulfinyl group and heterocyclic thio group may be substituted by the substituent group A.

Preferred examples of Z include hydrogen atom, halogen atom (e.g., fluorine atom, chlorine atom, bromine atom), unsubstituted arylthio group or arylthio group containing substituents such as halogen atom, alkyl group, alkoxy group, cyano group, aryloxycarbonyl group, alkoxycarbonyl group, ureido group, alkoxycarbonylamino group, acylamino group and carboxyl group (e.g., 2-(n-butoxy)-5-(t-octyloxy)-phenylthio, 2-(t-amylcarbonylamino)phenylthio, 2-(phenoxycarbonylamino)phenylthio, 2-(phenoxycarbonyl)-phenylthio, 2-(3,3-dimethylureido)phenylthio, pentafluorophenylthio, pentachlorophenylthio, 1,3,5-triisopropylphenylthio), unsubstituted arylsulfinyl group or arylsulfinyl group containing substituents such as halogen atom, alkyl group, alkoxy group, cyano group, alkoxycarbonyl group and carboxyl group (e.g., 2-(n-butoxy)-5-(t-octyloxy)phenylsulfinyl, 2-(t-amylcarbonylamino)phenylsulfinyl, 2-(phenoxycarbonylamino)phenylsulfinyl, 2-(phenoxycarbonyl)phenylsulfinyl, 2-(3,3-dimethylureido)phenylsulfinyl, pentafluorophenylsulfinyl, pentach-

lorophenylsulfinyl, 1,3,5-triisopropylphenylsulfinyl), unsubstituted heterocyclic thio group or heterocyclic thio group containing substituents such as halogen atom, alkyl group, alkoxy group, cyano group, alkoxycarbonyl group, carboxyl group and nitro group (e.g., pyrazolylthio, 5-nitro-2-pyridylthio) or nitroso group.

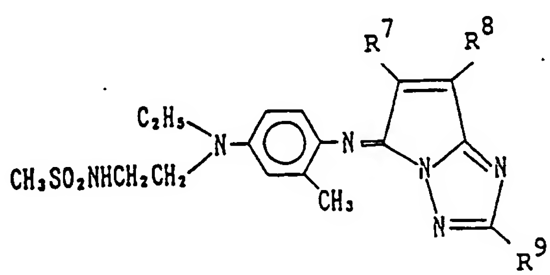
Preferred among these groups are hydrogen atom, arylthio group, and arylsulfinyl group.

The compound represented by formula (III) also indicates various compounds in equilibrium as shown below:



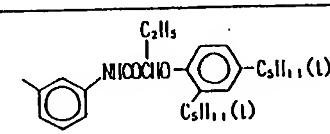
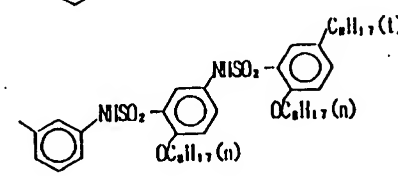
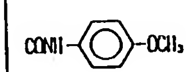
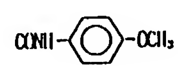
Specific examples of the compound of the present invention will be set forth below, but the present invention should not be construed as being limited thereto.

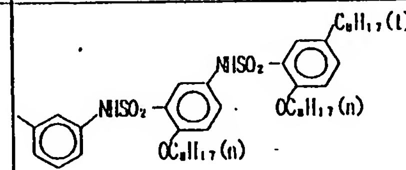
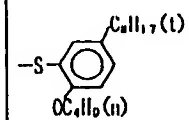
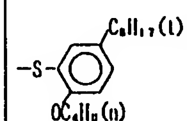
Firstly, specific examples of the compounds represented by formulae (I) and (III) will be given. In the structural formulae shown below, $(t)C_5H_{11}$ indicates $-C(CH_3)_2C_2H_5$, and $(t)C_8H_{17}$ indicates $-C(CH_3)_2CH_2C(CH_3)_3$. M^+ indicates the value (M^+) of the master peak of mass spectrum. λmax(nm) indicates the maximum absorption wavelength of ethyl acetate solution of a compound represented by formula (IV) when derived from the compound represented by formula (I):

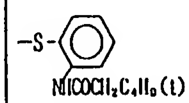
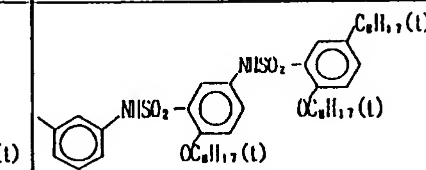
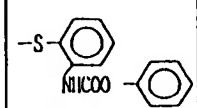
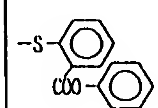
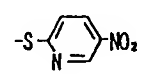


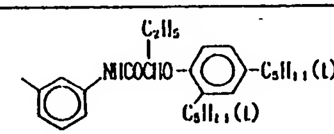
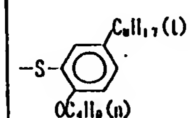
(IV)

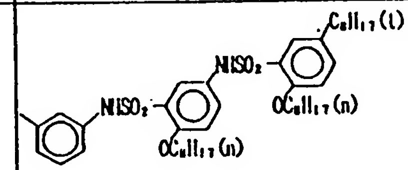
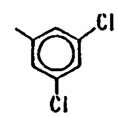
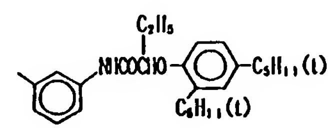
Some examples of the compound represented by formula (III) will be shown with their melting points (m.p.).

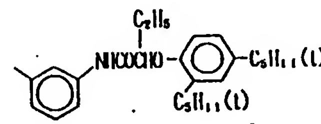
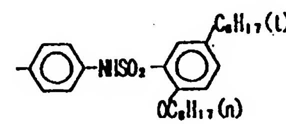
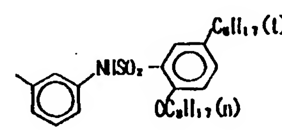
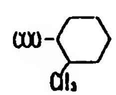
Comp. No.	R^8	M^+	R^7	Z	R^9 (nm) λmax	m.p.	λmax (nm)
III-1	CN	583	$COOCH_3$	H		104 °C	616
III-2	CN	1077	$COOCH_2CHC_4H_9(n)$ with C_2H_5	Cl		—	621
III-3	CN	1021	$COOC_4H_9(i)$	Cl	ditto	—	621
III-4	CN	1021	$COOC_4H_9(n)$	Cl	ditto	—	620
III-5	CN	1036		H	ditto	—	—
III-6	CN	1070		Cl	ditto	—	—
III-7	CN	1007	$COOC_3H_7(i)$	Cl	ditto	—	—

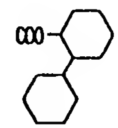
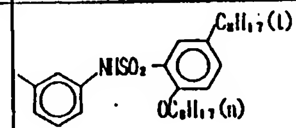
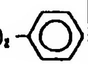
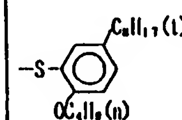
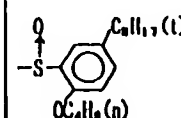
Comp. No.	R^8	M^+	R^7	Z	R^9	m.p.	λmax (nm)
III-8	CN	973	$COOC_3H_7$(i)	H		—	—
III-9	CN	1237	$COOCH_3$		ditto	130°C	—
III-10	CN	989	$COOCH_2CH_2OCH_3$	H	ditto	—	—
III-11	CN	987	$COOC_4H_9$(i)	H	ditto	200°C	—
III-12	CN	1043	$COOCH_2CH(C_2H_5)C_4H_9$(n)	H	ditto	127°C	—
III-13	CN	987	$COOC_4H_9$(n)	H	ditto	—	—
III-14	CN	1279	$COOC_4H_9$(n)		ditto	—	—

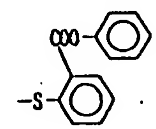
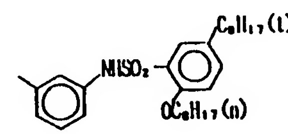
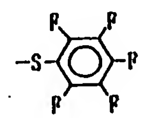
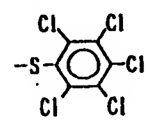
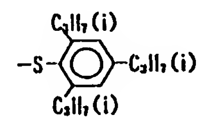
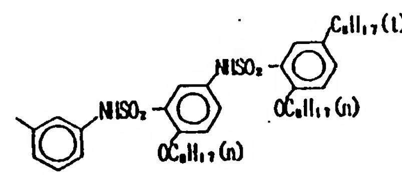
Comp. No.	R^6	M^+	R^7	Z	R^9 (nm) λmax	m.p.	λmax (nm)
III-15	CN	1208	$COOC_4H_9(i)$			205 °C	—
III-16	CN	1230	$COOC_4H_9(i)$		ditto	—	—
III-17	CN	1215	$COOC_4H_9(i)$		ditto	—	—
III-18	CN	1208	$COOC_4H_9(i)$		ditto	194 ~ 197°C	—
III-19	CN	1141	$COOC_4H_9(i)$		ditto	—	—

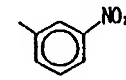
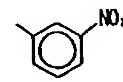
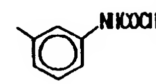
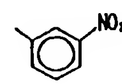
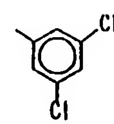
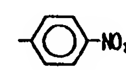
Comp. No.	R^8	M^+	R^7	Z	R^9	m.p.	λmax(nm)
III-20	CN	618	$COOCH_3$	Cl		146 °C	—
III-21	CN	876	$COOCH_3$		ditto	103 °C	—

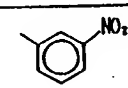
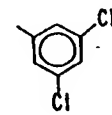
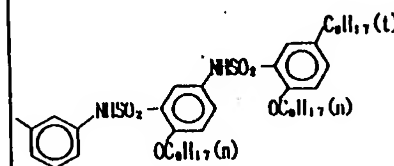
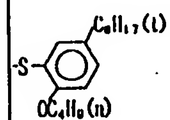
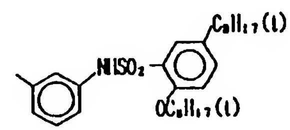
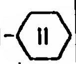
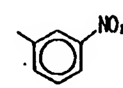
Comp. No.	R^8	M^+	R^7		R^9	m.p.	λmax (nm)
III-22	$COOC_2H_5$	959	CN	H		—	628
III-23	$COOCH_2CH(C_2H_5)C_4H_9(n)$	1043	CN	H	ditto	182 °C	—
III-24	$COOC_4H_9(i)$	987	CN	H	ditto	157 °C	630
III-25	$COOCH_2CH(C_6H_{13}(n))C_8H_{17}(n)$	545	CN	H		97 °C	629
III-26	$COOC_2H_5$	597	CN	H		114 °C	625

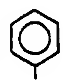
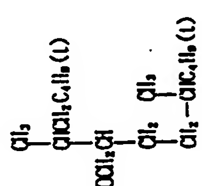
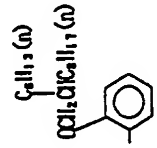
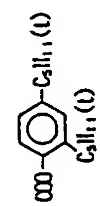
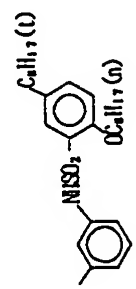
Comp. No.	R^8	M^+	R^7	Z	R^9	m.p.	λmax(nm)
III-27	$COOCH_2CH[CH(CH_3)CH_2C_4H_9(t)][CH_2CH_2CH(CH_3)CH_2C_4H_9(t)]$	822	CN	H		78 ℃	627
III-28	$COOC_2H_5$	675	CN	H		—	624
III-29	$COOC_2H_5$	675	CN	H		240 ℃	629
III-30	$COOCH_2CH[CH(CH_3)CH_2C_4H_9(t)][CH_2CH_2CH(CH_3)CH_2C_4H_9(t)]$	900	CN	H	ditto	—	640
III-31	$COOC_{14}H_{29}(n)$	844	CN	H	ditto	180 ℃	—
III-32		743	CN	H	ditto	>250℃	—

Comp. No.	R^8	M^+	R^7	Z	R^9 λmax (nm)	m.p.	λmax (nm)
III-33		812	CN	H		144 °C	—
III-34	$COOCH_2CH_2SO_2$- 	816	CN	H	ditto	129 °C	—
III-35	$COOCH_2CH_2-(CF_2)_6F$	993	CN	H	ditto	194 °C	638
III-36	$COOCH_2-(CF_2)_3H$	801	CN	H	ditto	162 °C	646
III-37	$COOC_2H_5$	968	CN		ditto	181 °C	—
III-38	$COOC_2H_5$	984	CN		ditto	142 °C	—

Comp. No.	R^6	M^+	R^7	Z	R^9	m.p.	λmax (nm)
III-39	$COOC_2H_5$	815	CN			228 °C	—
III-40	$COOC_2H_5$	817	CN		ditto	108 ~ 110°C	—
III-41	$COOC_2H_5$	900	CN		ditto	—	—
III-42	$COOC_2H_5$	909	CN		ditto	194 ~ 196°C	—
III-43	CN	914	$COOCH_3$	H		212 °C	620

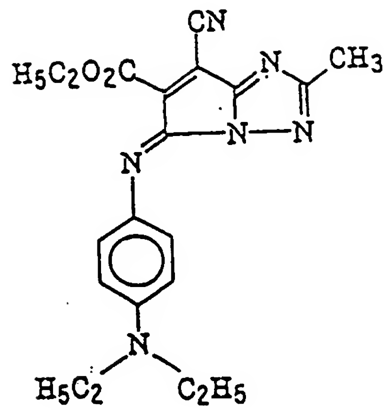
Comp. No.	R^8	M^+	R^7	Z	R^9 (nm) λmax	m.p.	λmax (nm)
III-44	CN	278	CN	H		—	—
III-45	$COOC_2H_5$	325	CN	H		—	629
III-46	$COOC_2H_5$	337	CN	H		250 °C	—
III-47	CN	311	$COOCH_3$	H		—	—
III-48	$COOC_2H_5$	348	CN	H		—	628
III-49	$COOC_2H_5$	325	CN	H		—	—

Comp. No.	R^8	M^+	R^7	Z	R^9	m.p.	λmax (nm)
III-50	$CONH_2$	296	CN	H		—	611
III-51	CN	334	$COOCH_3$	H		205 ~ 208°C	619
III-52	CN	1023	$COOCH_2CH_2OCH_3$	Cl		143 ~ 145°C	635
III-53	CN	1335	$COOCH_2CH(C_2H_5)C_4H_9(n)$		ditto	—	—
III-54	$COOC_2H_5$	710	CN	Cl		—	—
III-55	CONH- 	378	CN	H		—	611

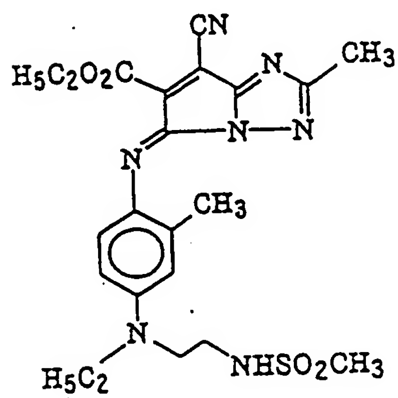
Comp. No.	R^8	M^+	R^7	Z	R^9	m.p.	λmax
III-56	$COOC_2H_5$	280	CN	H		—	621
III-57		504	CN	H		—	624
III-58	$COOCH_3$	506	CN	H		—	—
III-59		808	CN	H		—	644

Specific examples of the compounds represented by formulae (I) and (II) will be given below. In the structural formulae shown below, Ph represents a phenyl group.

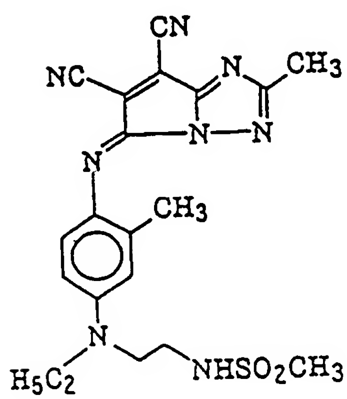
(I-1)



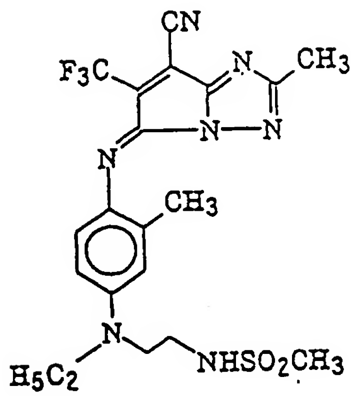
(I-2)



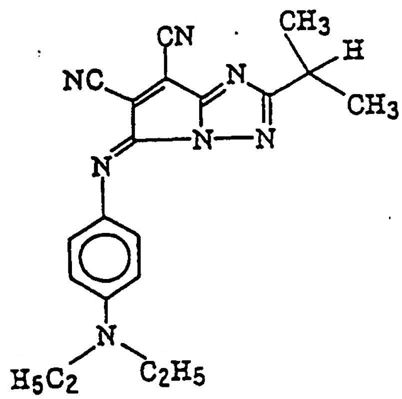
(I-3)



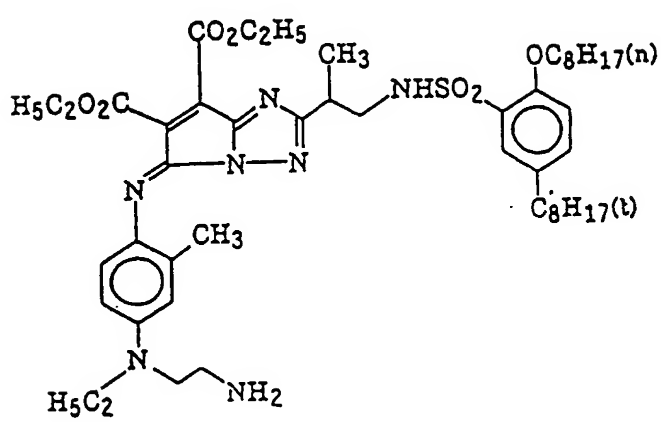
(I-4)



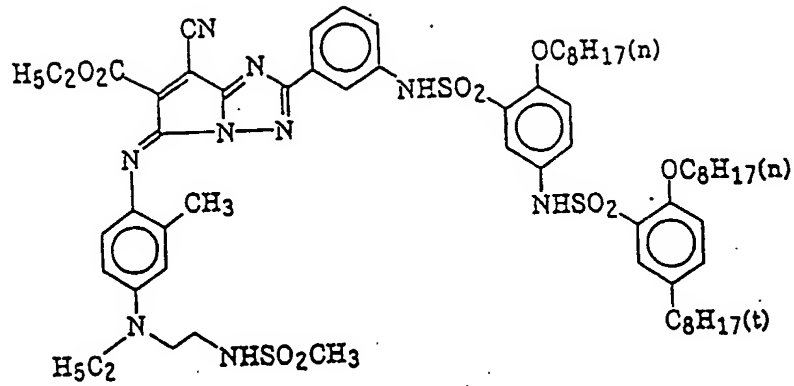
(I-5)



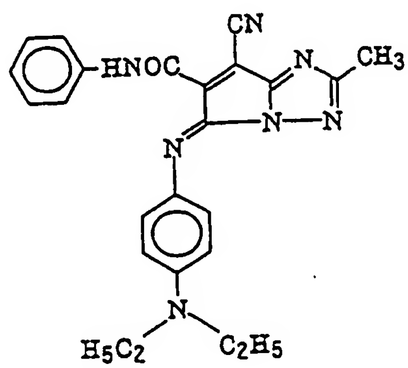
(I-6)



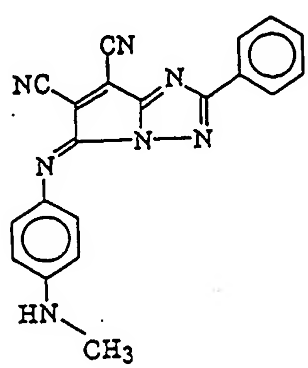
(I-7)


CN
H5C2O2C
N
N
N
N
NHSO2
OC8H17(n)
CH3
NHSO2
OC8H17(n)
C8H17(t)
N
H5C2
NHSO2CH3

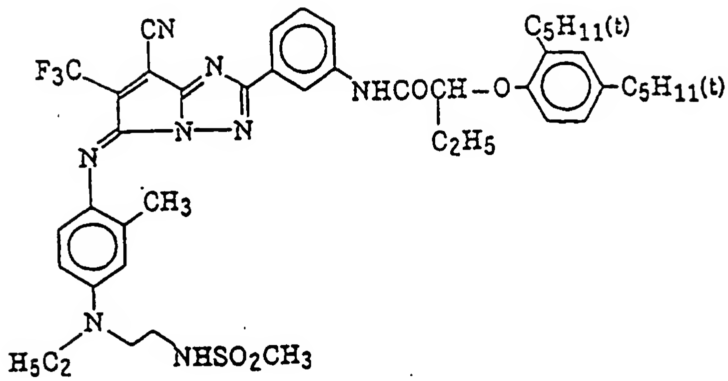
(I-8)


CN
HNOC
N
CH3
N
N
N
N
H5C2
C2H5

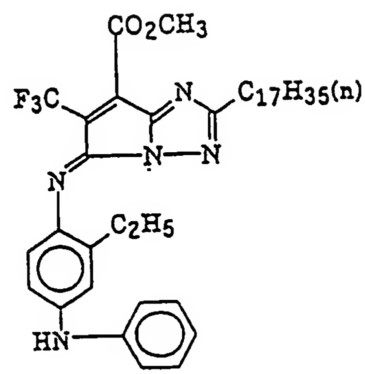
(I-9)


CN
NC
N
N
N
N
HN
CH3

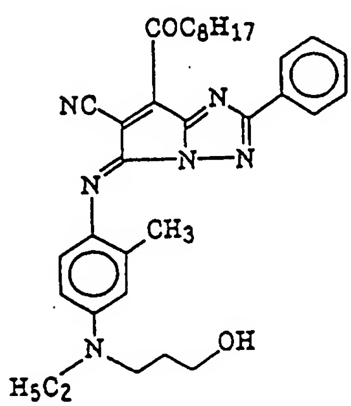
(I-10)



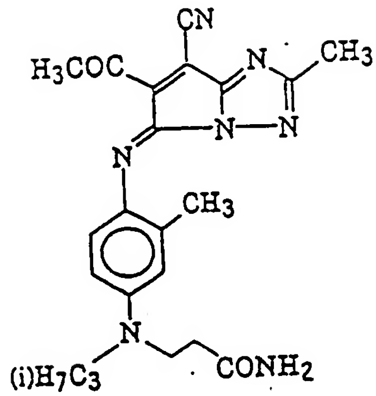
(I-11)



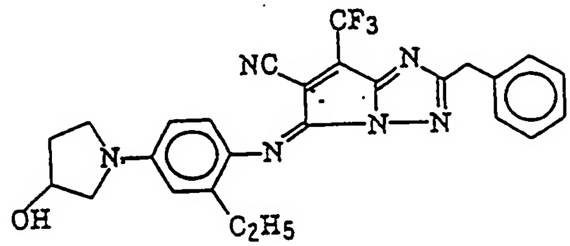
(I-12)



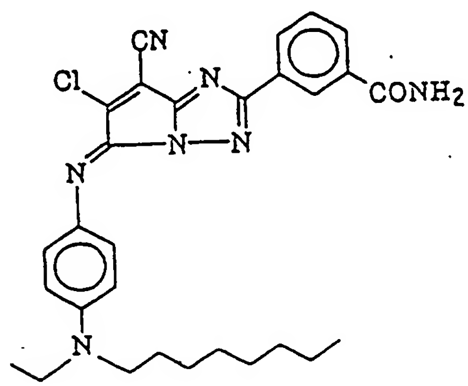
(I-13)


CN
H3COC
N
CH3
N
N
N
CH3
N
(i)H7C3
CONH2

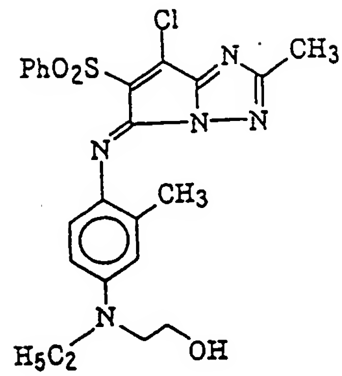
(I-14)


CF3
NC
N
N
N
N
N
OH
C2H5

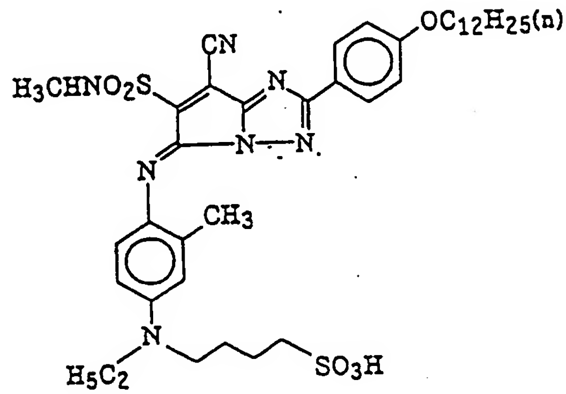
(I-15)


CN
Cl
N
N
N
CONH2
N
N

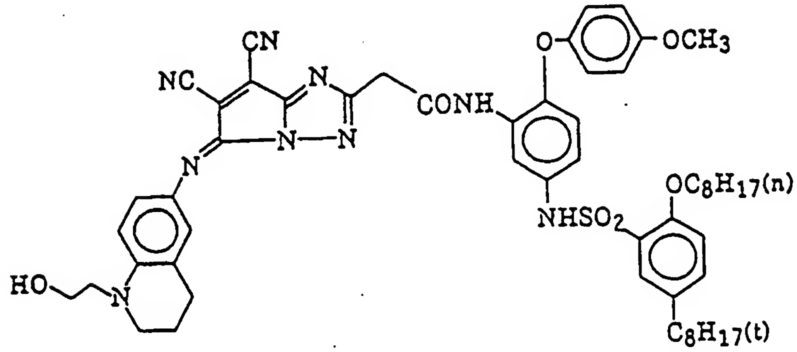
(I-16)



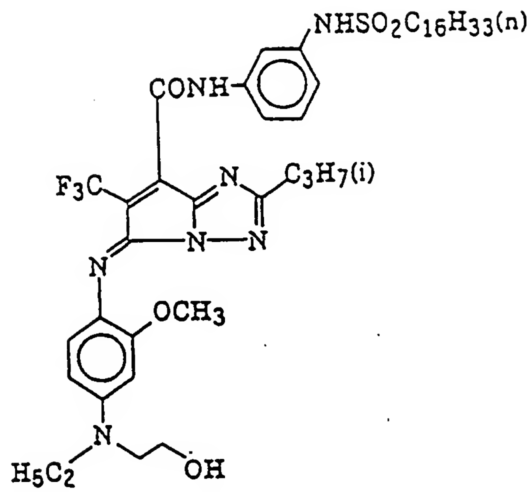
(I-17)



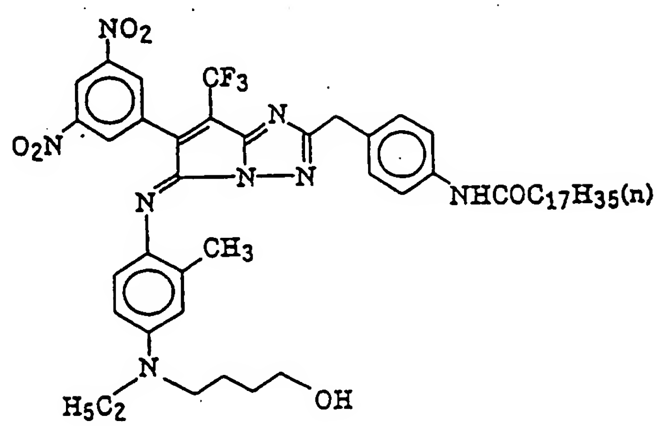
(I-18)



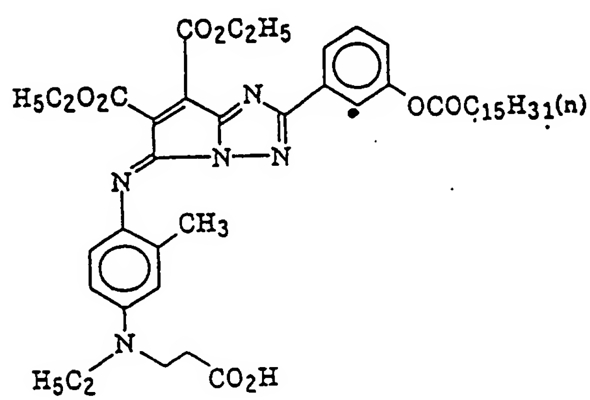
(I-19)



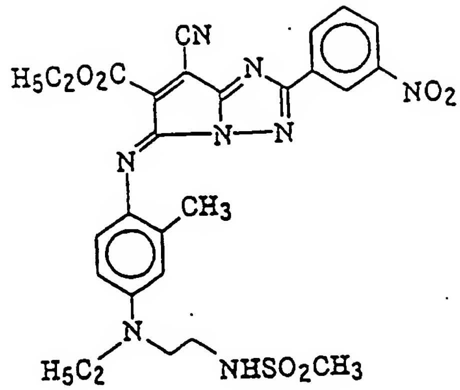
(I-20)



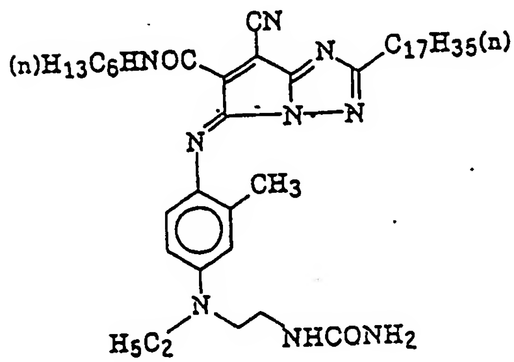
(I-21)



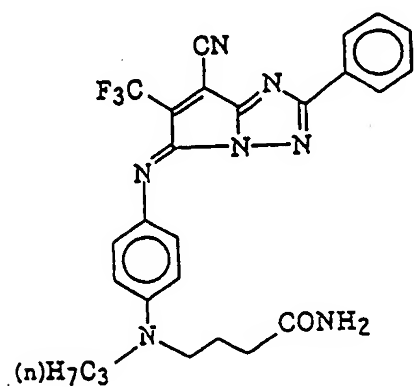
(I-22)


CN
$H_5C_2O_2C$
N
N
N
N
NO_2
N
CH_3
N
H_5C_2
$NHSO_2CH_3$

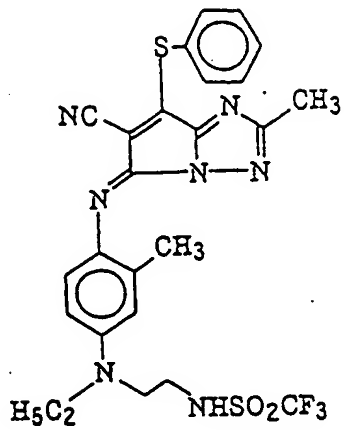
(I-23)


CN
$(n)H_{13}C_6HNOC$
N
$C_{17}H_{35}(n)$
N
N
N
CH_3
N
H_5C_2
$NHCONH_2$

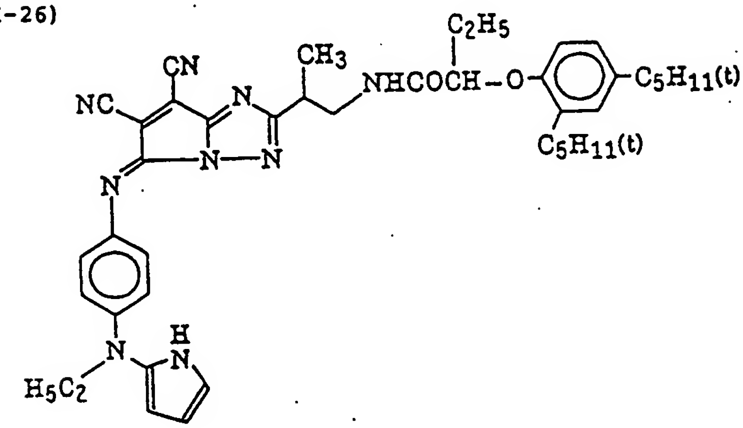
(I-24)


CN
F_3C
N
N
N
N
N
$CONH_2$
$(n)H_7C_3$

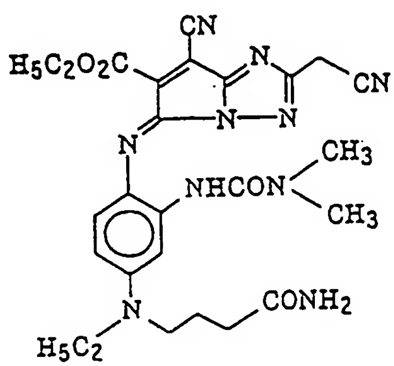
(I-25)



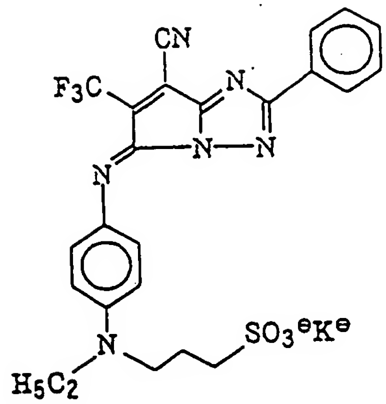
(I-26)



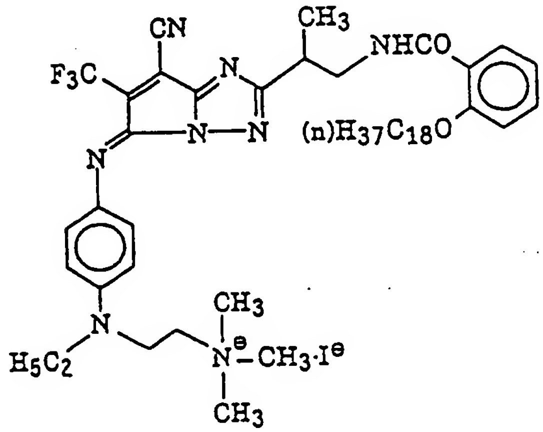
(I-27)



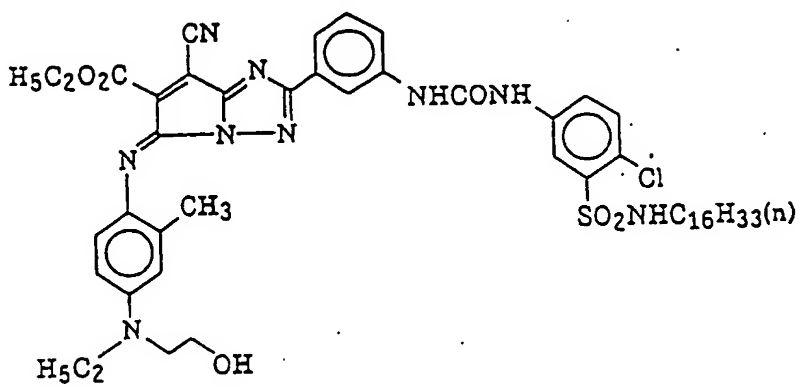
(I-28)



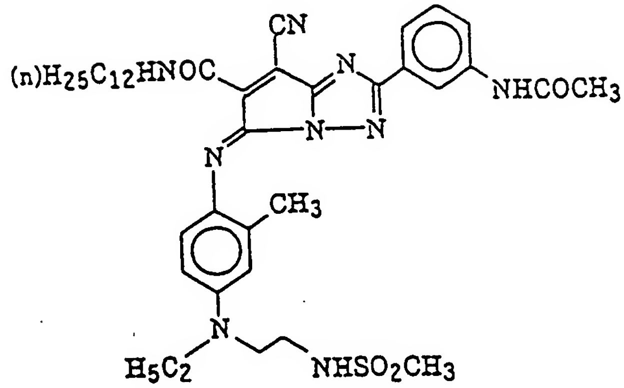
(I-29)



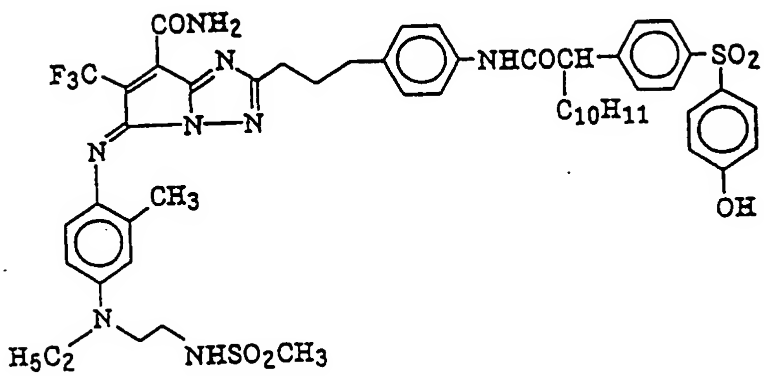
(I-30)



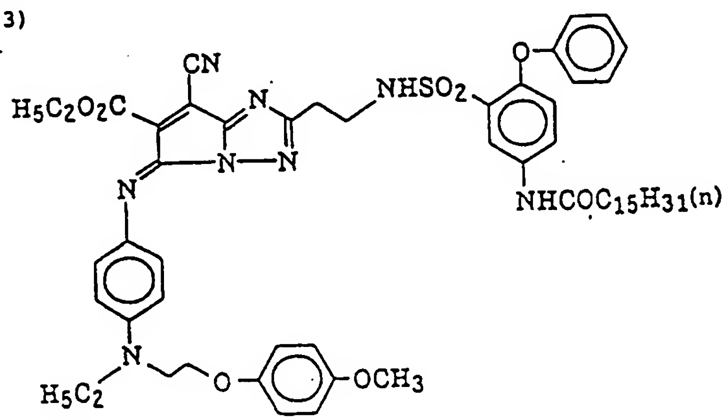
(I-31)



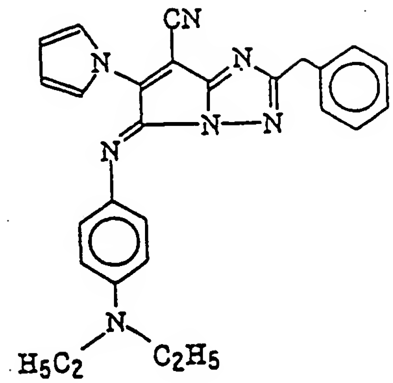
(I-32)



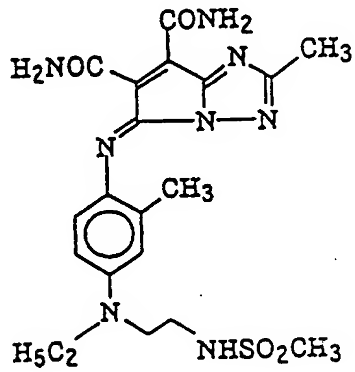
(I-33)



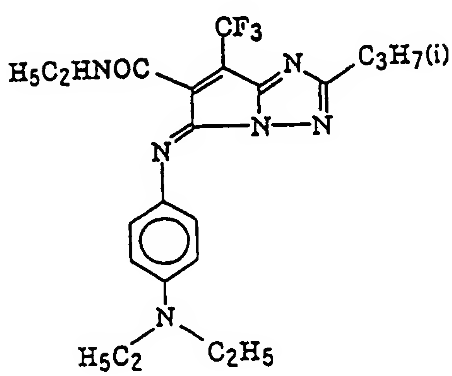
(I-34)



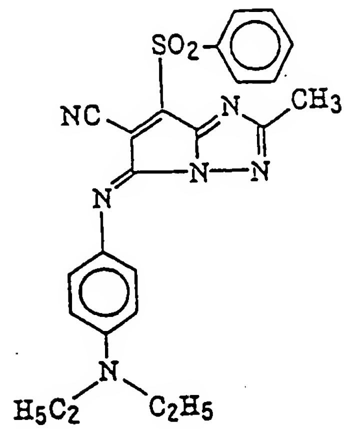
(I-35)



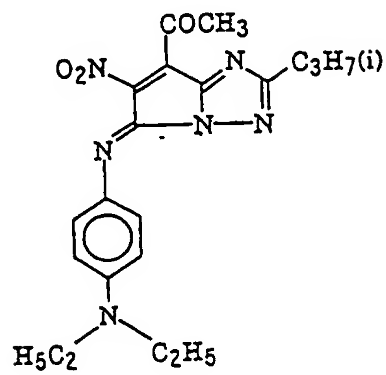
(I-36)



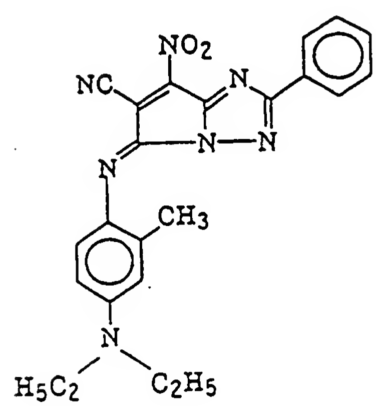
(I-37)


SO2
NC
N
CH3
N
N
N
N
H5C2
C2H5

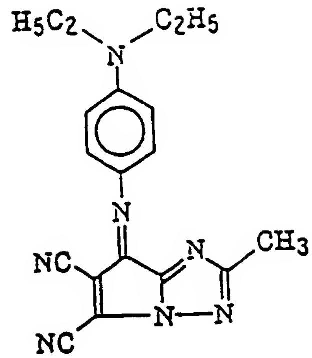
(I-38)


COCH3
O2N
N
C3H7(i)
N
N
N
N
H5C2
C2H5

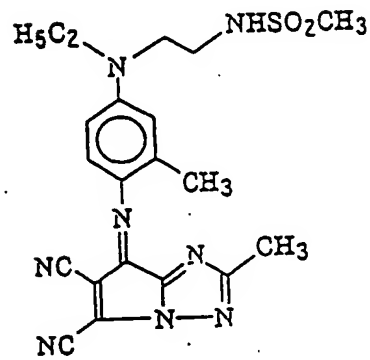
(I-39)


NO2
NC
N
N
N
N
CH3
N
H5C2
C2H5

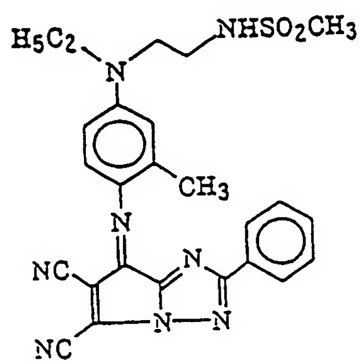
(II-1)



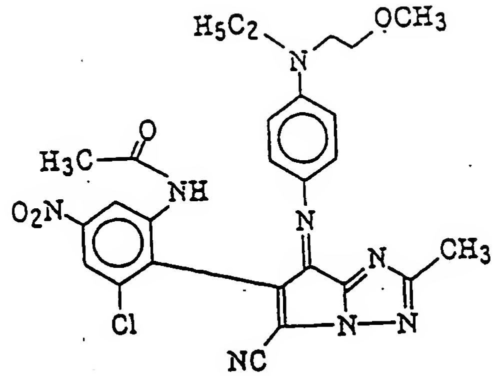
(II-2)



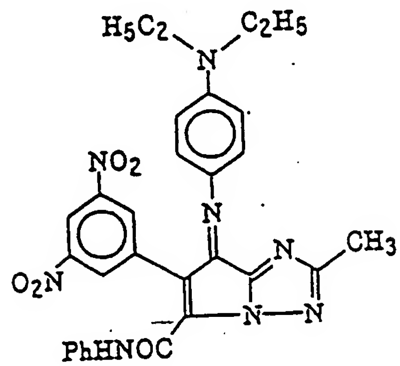
(II-3)



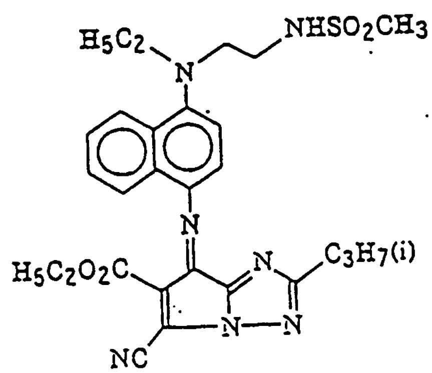
(II-4)



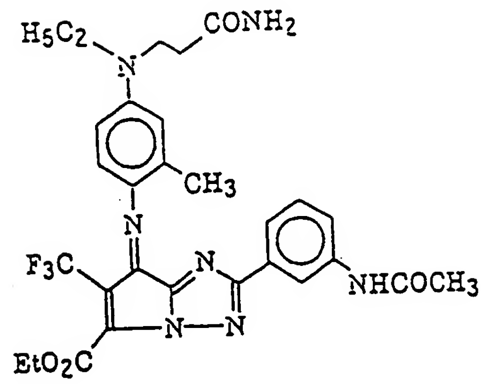
(II-5)



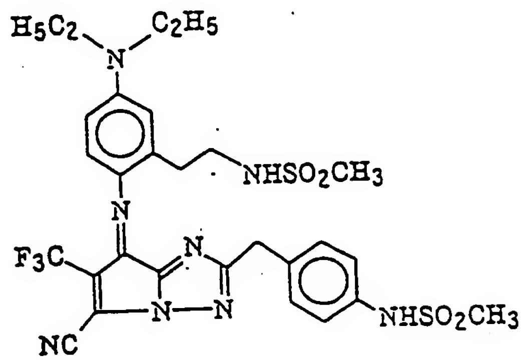
(II-6)



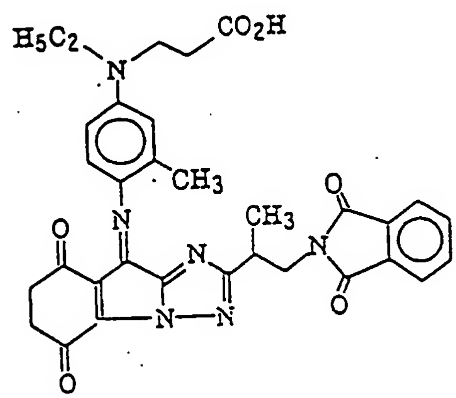
(II-7)



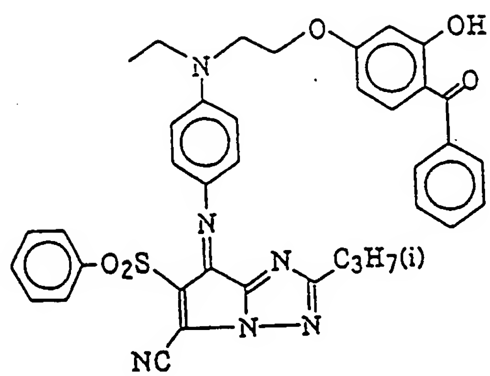
(II-8)



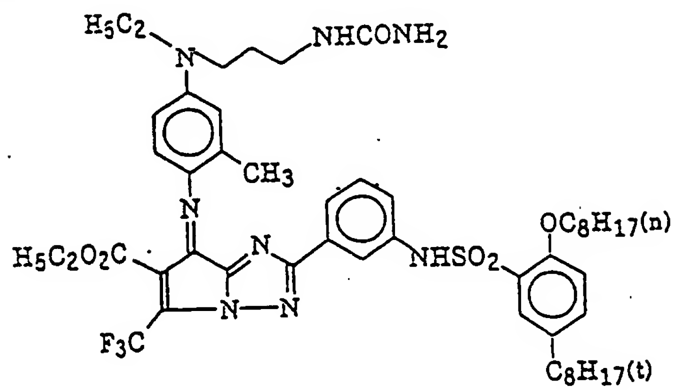
(II-9)



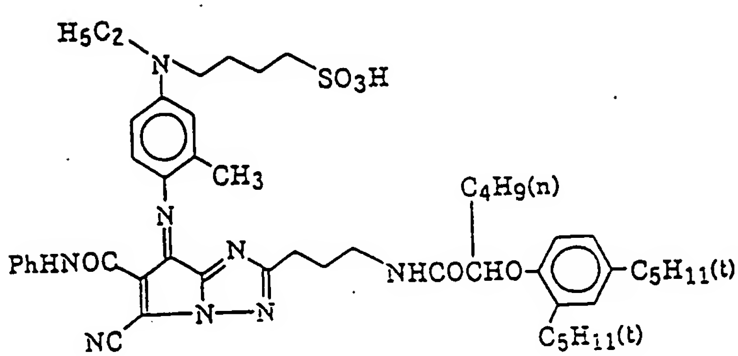
(II-10)



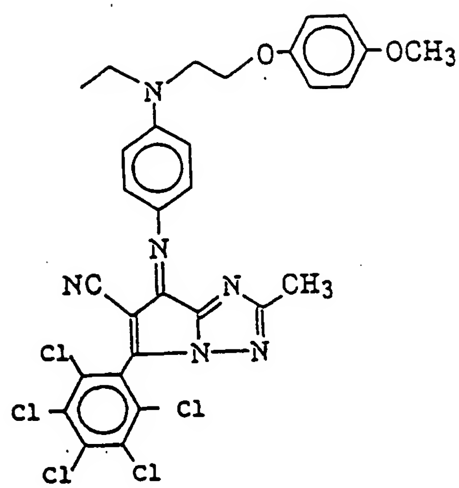
(II-11)



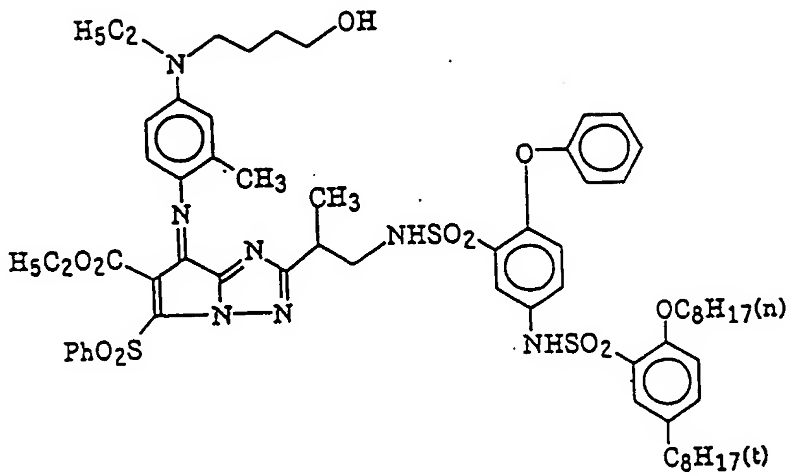
(II-12)



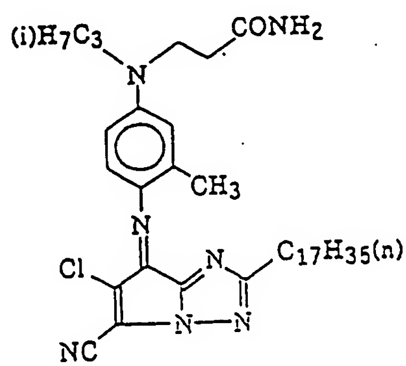
(II-13)



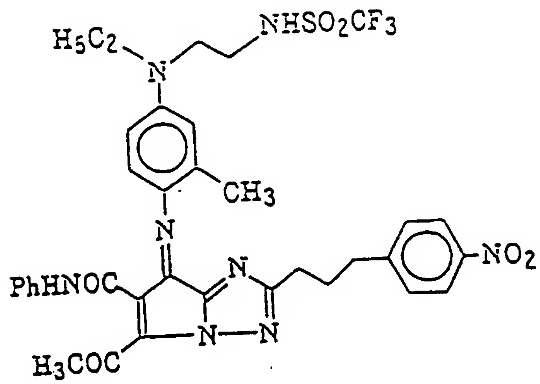
(II-14)



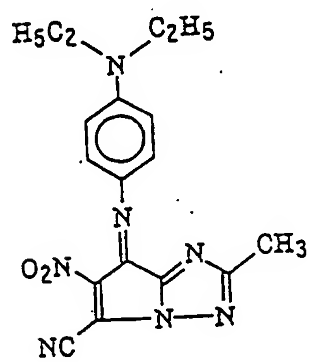
(II-15)



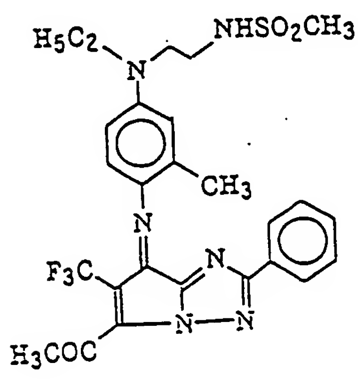
(II-16)



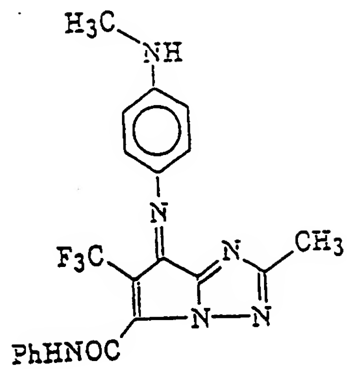
(II-17)



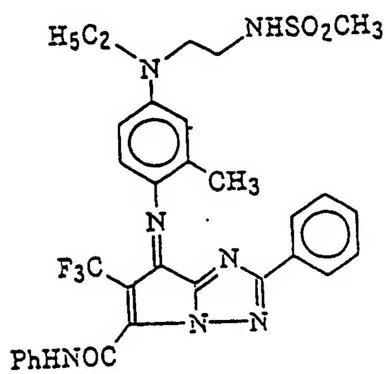
(II-18)



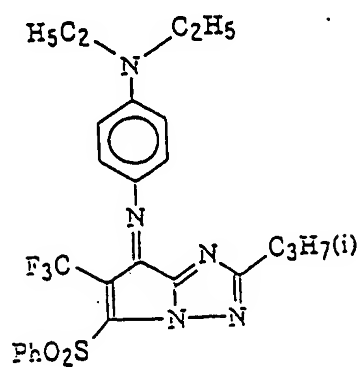
(II-19)



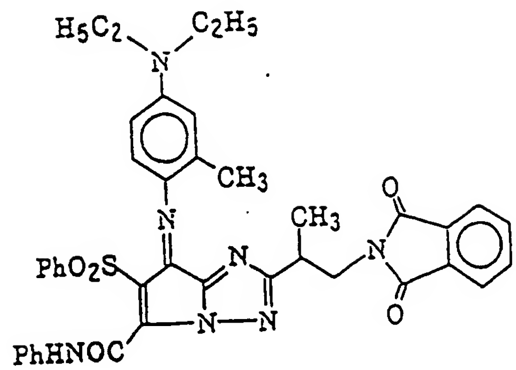
(II-20)



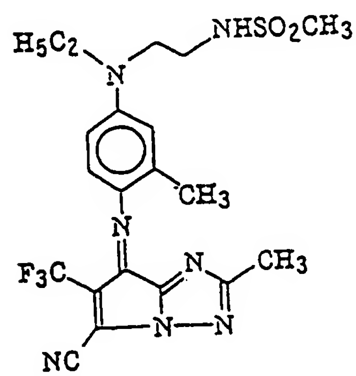
(II-21)



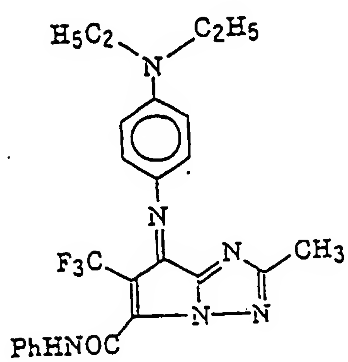
(II-22)



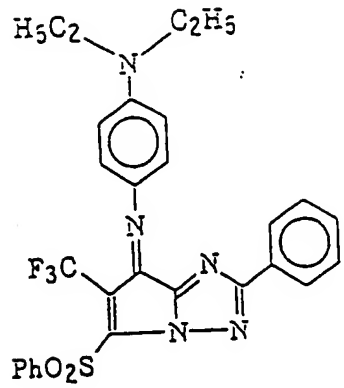
(II-23)



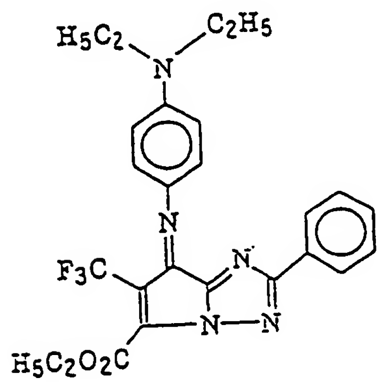
(II-24)



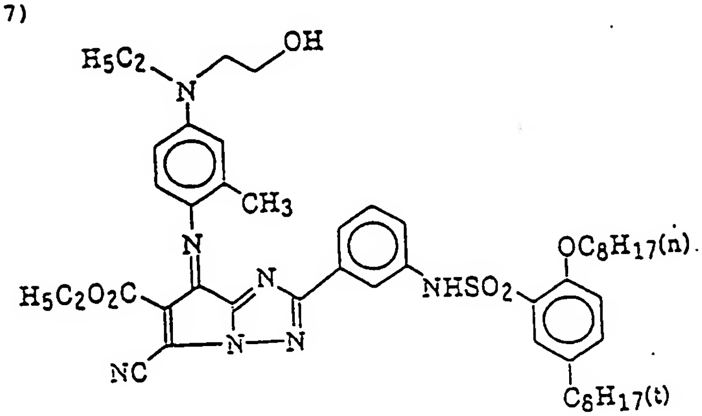
(II-25)



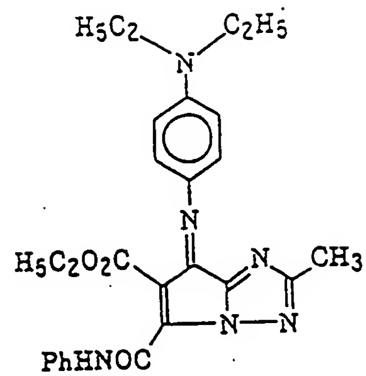
(II-26)



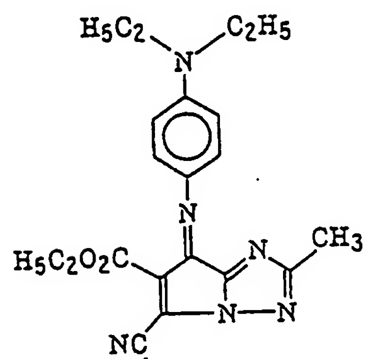
(II-27)



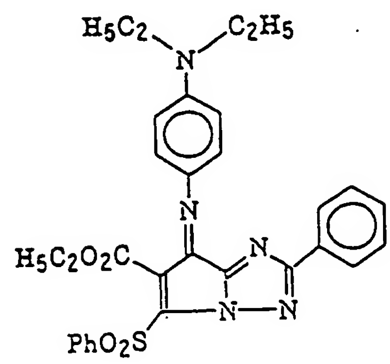
(II-28)



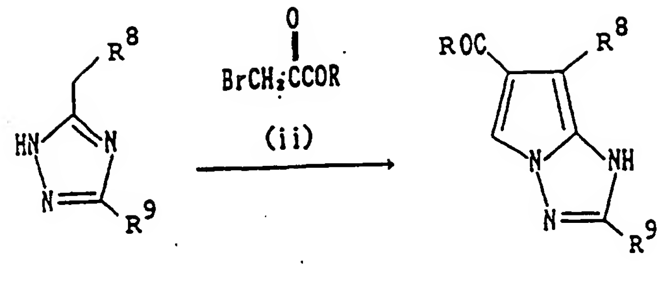
(II-29)



(II-30)

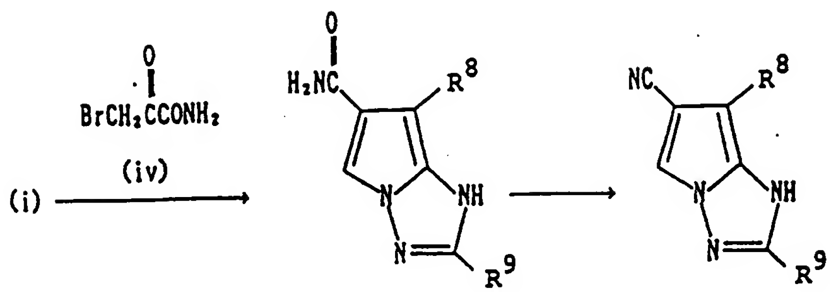


Typical examples of process for the synthesis of the compound represented by formula (III) will be given below. When R^7 = COR:

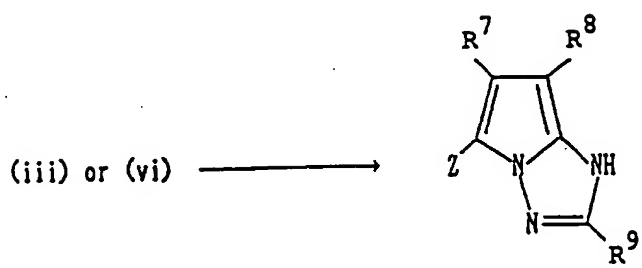


(i) (iii)

When R^7 = CN:



(v) (vi)



(III)

Compound (i) can be synthesized by any known method. For example, synthesis methods as described in J. C. S., 518 (1961), J. C. S., 5149 (1962), Angew. Chem., 72,956 (1960), and Berichte., 97,3436 (1964), and references cited therein, and analogous methods can be used.

The synthesis of Compound (iii) can be accomplished by the nucleophilic displacement reaction from Compound (i) to Compound (ii) and the subsequent cyclization reaction.

In this synthesis, a base such as sodium hydride, triethylamine, diazabicycloundecene, potassium carbonate and sodium carbonate may be preferably used. The reaction may be effected free of solvent or in a solvent such as tetrahydrofuran, acetonitrile, N,N-dimethylformamide, N,N-dimethylacetamide, N,N'-dimethylimidazolidon-2-one, acetone and toluene. The reaction temperature is normally in the range of

-20 °C to 150 °C, preferably 0 °C to 100 °C.

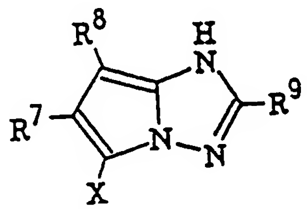
The synthesis of Compound (v) can be accomplished by the nucleophilic displacement reaction from Compound (i) to Compound (iv) and the subsequent cyclization reaction as in the synthesis of Compound (iii).

Compound (vi) is derived by the dehydration reaction of Compound (v). In this reaction, phosphorus oxychloride, phosphorus pentachloride, phosphorus trichloride, etc. may preferably be used. The reaction may be effected free of solvent or in toluene or chloroform. The reaction temperature is normally in the range of - 10 °C to 250 °C, preferably 20 °C to 200 °C.

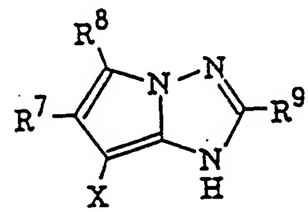
The compound represented by formula (III) can be synthesized from Compound (iii) or (vi) by a known method.

For example, if an arylthio group or heterocyclic thio group is connected to Compound (III) to obtain a 7-aromatic mercapto or heterocyclic mercapto substituted compound, a method described in U.S. Patent 3,227,554 can be used, i.e., a process can be used which comprises dissolving an aryl-mercaptan, heterocyclic mercaptan and their disulfides in a halogenated hydrocarbon solvent, treating the solution with chlorine or sulfuryl chloride to produce sulfenyl chloride, and then adding the solution to a solution of Compound (III) in an arotonic polar solvent.

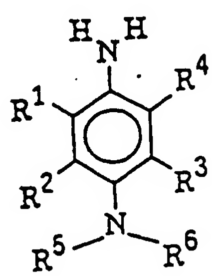
The compounds represented by formulae (I) and (II) can be synthesized by oxidation coupling of the following Compound A or B with the following Compound C:



(A)



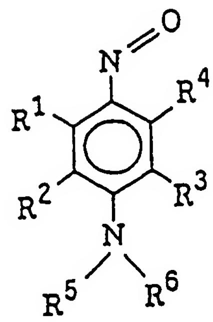
(B)



(C)

In these formulae, X represents a hydrogen atom or split-off group which splits off upon coupling reaction, and formula (A) includes formula (III). It goes without saying that Compounds A and B may be in the form of their tautomers.

Alternatively, the compounds represented by formulae (I) and (II) can be synthesized by the dehydration condensation of the above mentioned Compound A or B with the following Compound D:



(D)

In this case, X in Compounds A and B is a hydrogen atom.

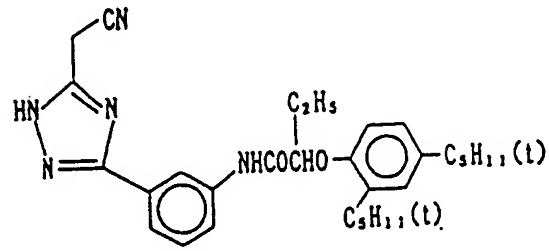
For example, the compound represented by formula (I) can be derived from the compound represented by formula (III) by a known method as described in JP-A-63-145281. That is, the compound represented by formula (I) can be synthesized in the presence of a compound represented by formula (III), a phenylenediamine, and an oxidizer.

It is thought that this coupling reaction involves a nucleophilic attack of a coupler anion on quinodimine produced by the oxidation of phenylenediamine to form a leuco dye which is then converted to an azomethine dye as described in T. H. James, The Theory of the Photographic Process, 4th ed., Macmillan, 1977. The reaction preferably proceeds under a basic condition. The reaction medium may be any of an organic medium, aqueous organic medium and aqueous solution. If the reaction is effected in a basic aqueous solution, the compound represented by formula (III) may be an oil-in-water dispersion. The oil-in-water dispersion may be present in a hydrophilic colloidal medium such as gelatin. As the oxidizer there may be used any organic or inorganic oxidizer having a potential strong enough to oxidize phenylenediamine. The oxidizer may be used in the form of solution or dispersion in the reaction medium. If Z in formula (III) is a hydrogen atom, phenylenediamine is present in the system in an amount of 0.1 to 10 mol, preferably 0.5 to 2 mol per mol of compound of formula (III), and the oxidizer is used in an amount of at least 4 equivalents, preferably 4.4 to 20 equivalents. If Z is not a hydrogen atom, the compound represented by formula (I) can be synthesized in the same manner as above except that the oxidizer is used in an amount of at least 2 equivalents, preferably 2.2 to 10 equivalents. If the reaction medium is aqueous, coupling may be effected at a pH of 8 or more, preferably 10 to 12. As the oxidizer there can be used silver halide, hydrogen peroxide, manganese dioxide, potassium persulfate, oxygen, or compounds as described in Fieser & Fieser, Organic Reagents.

The present invention will be further described in the following examples, but the present invention should not be construed as being limited thereto.

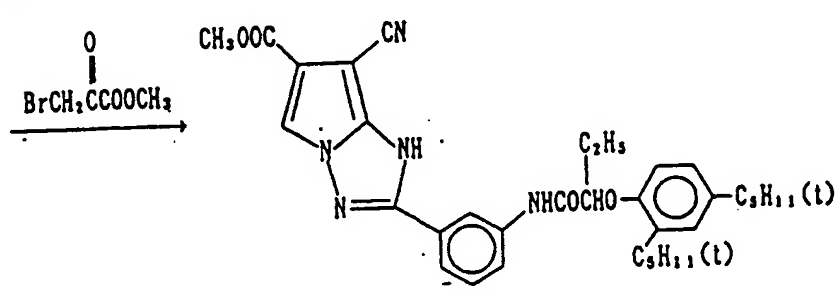
EXAMPLE 1: Synthesis of Compound (III-1)

Compound (III-1) was synthesized in the following process:



(a)

(b)

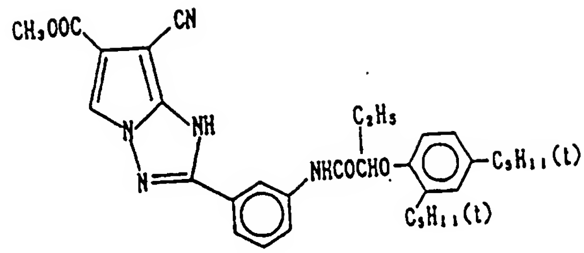


(III-1)

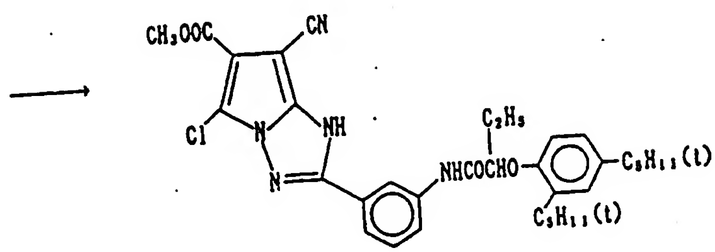
To a solution of Compound (a) (50.1 g; 0.1 mol) and Compound (b) (19.9 g; 0.11 mol) in tetrahydrofuran (300 ml) was added gradually sodium hydride (12.0 g; 0.30 mol) at a temperature of 0 °C in such a manner that the reaction temperature didn't rise. The reaction system was stirred for 1 hour. 200 ml of a 1 N dilute hydrochloric acid was added to the reaction system. The reaction system was extracted with 300 ml of ethyl acetate three times. The resulting organic phase was washed with water and saturated brine, and then dried over anhydrous sodium sulfate. The solvent was distilled off under reduced pressure. The material was purified through column chromatography (developing solvent: 3 : 1 mixture of hexane and ethyl acetate) to obtain 7.57 g of Compound (III-1) (yield: 13%).

EXAMPLE 2: Synthesis of Compound (III-22)

Compound (III-22) was synthesized in the following process:



(III-1)

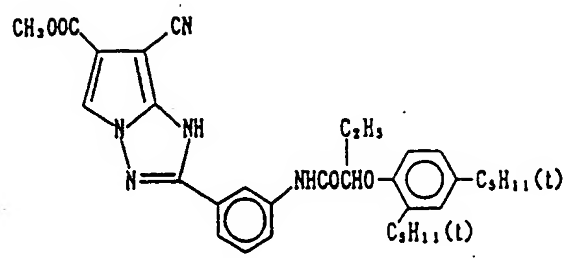


(III-20)

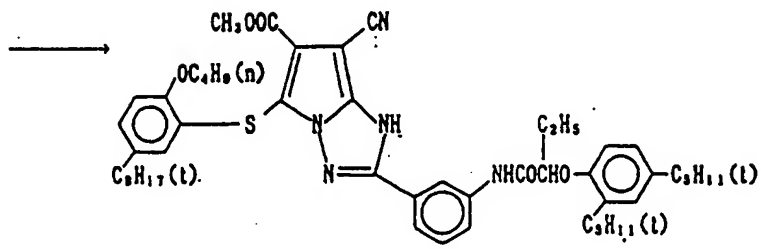
To a solution of Compound (III-1) (2.91 g; 5 mmol) in methylene chloride (30 ml) was added dropwise sulfuryl chloride (0.74 g; 5.5 mmol) at a temperature of 0°C. The reaction system was stirred for 1 hour. Water was added to the reaction system. The reaction system was extracted with 30 cc of methylene chloride three times. The resulting organic phase was washed once with saturated brine, and then dried over anhydrous sodium sulfate. The solvent was distilled off under reduced pressure. The material was recrystallized from acetonirile to obtain 2.83 g of Compound (III-20) (yield: 92%).

EXAMPLE 4: Synthesis of Compound (III-21)

Compound (III-21) was synthesized in the following process:



(III-1)

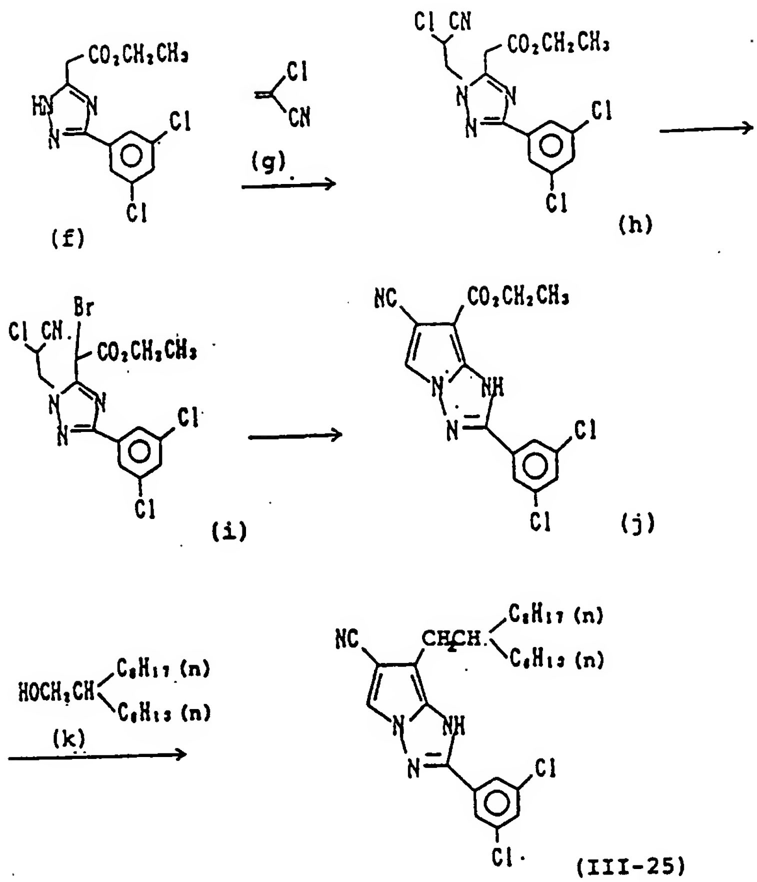


(III-21)

To a solution of di-[(2-n-butoxy-5-t-octyl)phenyl]disulfide (3.53 g; 6 mmol) in methylene chloride (20 ml) was added sulfuryl chloride (1.76 g; 13 mmol) at a temperature of 0° C. The reaction system was stirred for 1 hour. Methylene chloride and sulfuryl chloride were removed under reduced pressure. To the residue was added methylene chloride (20 ml). The solution was added dropwise to a solution of Compound (III-1) (2.91 g; 5 mmol) in N,N-dimethylformamide (10 ml) at a temperature of 0° C. The reaction system was stirred for 1 hour. Water was added to the reaction system. The reaction system was extracted with 30 ml of ethyl acetate twice. The resulting organic phase was washed with water and saturated brine, and then dried over anhydrous sodium sulfate. The solvent was distilled off under reduced pressure. The material was purified through silica gel chromatography (developing solvent: 2 : 1 mixture of hexane and ethyl acetate) to obtain 2.93 g of Compound (III-21) (yield: 67%).

EXAMPLE 5: Synthesis of Compound (III-25)

Compound (III-25) was synthesized in the following process:



30.0 g of Compound (f) and 11.4 g of Compound (g) were dissolved in 300 ml of tetrahydrofuran. 6.0 ml of tetramethyl guanidine was added to the solution. The material was stirred at room temperature for 5 hours. 500 ml of ethyl acetate was added to the material. The material was then washed with water. The ethyl acetate was dried, and then distilled off. The material was then crystallized from methanol to obtain 27.5 g of Compound (h).

27.4 g of Compound (h) thus obtained was dissolved in 270 ml of tetrahydrofuran. 13.6 g of bromine was gradually dropwise added to the solution under cooling with ice. The material was stirred for 5 hours. 500 ml of ethyl acetate was added to the material. The material was then washed with water until it turned neutral. The resulting ethyl acetate phase was dried, and then distilled off. The residue was purified through column chromatography to obtain 28.0 g of Compound (i).

28.0 g of Compound (i) thus obtained was dissolved in 170 ml of tetrahydrofuran. 9.6 g of 60% sodium hydride was gradually added to the material while the reaction temperature was kept at - 10°C. After the completion of the reaction, ethyl acetate was added to the reaction system. The material was then washed with water. The resulting ethyl acetate phase was dried, and then distilled off. The material was purified through column chromatography to obtain 3.0 g of Compound (j).

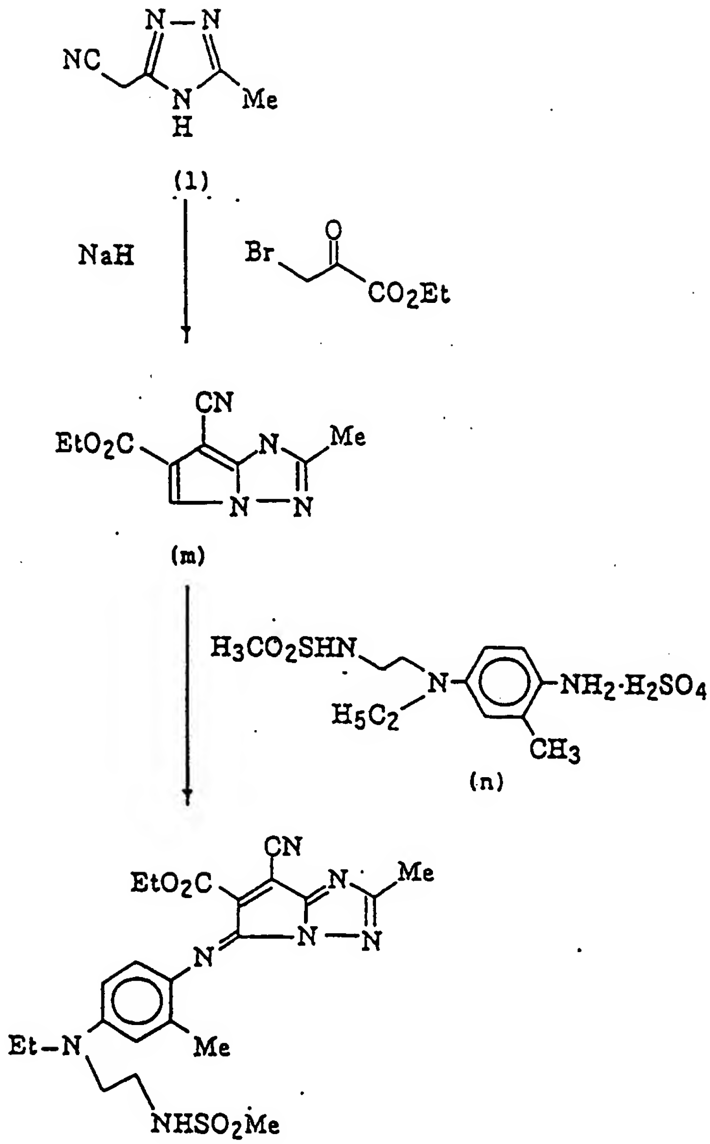
1.8 g of Compound (j) thus obtained and 12.4 g of Compound (k) were dissolved in 2.0 ml of sulfolane. To the solution was further added 1.5 g of titanium isopropoxide. The reaction system was then allowed to undergo reaction for 1.5 hours while the reaction temperature was kept at 110°C. Ethyl acetate was then added to the material. The material was then washed with water. The resulting ethyl acetate phase was dried, and then distilled off. The residue was then puridied through column chromatography to obtain 1.6 g of Compound (III-25).

The melting point of Compound (III-25) was 97 to 98°C.

EXAMPLE 6: Synthesis of Dye of Compound (III-20)

To a solution of Compound (III-20) (9.59 g; 10.0 mmol) in 100 ml of a 1 : 1 mixture of ethyl acetate and ethanol was added 40 ml of an aqueous solution of sodium carbonate (9 g). Subsequently, 4-(N-ethyl-N-(2-methanesulfonamidoethyl)amino)-2-methylaniline sulfate (6.38 g; 12.2 mmol) was added to the system. The material was then stirred at room temperature for 5 hours. To the material was then added dropwise 20 ml of an aqueous solution of ammonium persulfate (4.5 g). The material was then stirred for 1 hour. The material was then extracted with ethyl acetate three times. The resulting organic phase was washed with saturated aqueous solution of sodium chloride, and then dried over anhydrous sodium sulfate. The solvent was then distilled off under reduced pressure. The material was then purified through column chromatography (developing solvent: 20 : 1 mixture of methylene chloride and methanol). The material was then recrystallized from methanol to obtain 10.2 g of a dye of Compound (III-20) (yield: 83%).

EXAMPLE 7: Synthesis of Compound (I-2)



(I-2)

1.5 g of 3-cyanomethyl-5-methyl-1,2,4-triazole (Compound (ℓ)) was dissolved in 30 ml of tetrahydrofuran. To the solution was added 1.0 g (24.6 mmol) of sodium hydride (60% in oil). The material was then heated to a temperature of 50°C. To the material was added 1.9 ml (14.7 mmol) of ethyl bromopyruvate. The material was further heated under reflux for 2 hours. The material was then cooled to room temperature. To the material were then added brine and 2 N hydrochloric acid solution to acidify the solution. The material was extracted with ethyl acetate twice, and then dried. Ethyl acetate was then distilled off under reduced pressure. The residue was then purified through silica gel chromatography to obtain 1.20 g of Compound (m) (yield: 45%).

The synthesis of Compound (ℓ) was accomplished by a method described in Journal of the Chemical Society, 5149 (1962).

To 1.0 g of Compound (m), 20 cc of ethyl acetate, 20 cc of ethanol, 24 cc of water, 6.6 g of sodium carbonate and 3.1 g of Compound (n) was added a solution of 4.6 g of ammonium persulfate in 5 cc of water with stirring.

The reaction system was then allowed to undergo reaction at a temperature of 20 °C for 1 hour. The material was then extracted with ethyl acetate. The resulting organic phase was washed with water twice, and then dried over magnesium sulfate. After filtration, the solvent was distilled off. The resulting crude crystal was purified through silica gel chromatography, and then recrystallized from methanol to obtain 0.82 g of Compound (I-2) (yield: 37%; m.p. 223 to 224 °C)

The absorption characteristics of Compound (I-2) of the present invention in a solvent are shown in Fig. 1 together with those of Comparative Dye a.

In Fig. 1, the solid line indicates the absorption characteristics of Compound (I-2) of the present invention, and the broken line indicates the absorption characteristics of Comparative Dye a.

The maximum absorption wavelength (λmax) and half-value width of Compound (I-2) of the present invention and Comparative Dye a are set forth below.

Compound (I-2) of the present invention

λmax: 602.3 nm (in ethyl acetate)
Half-value width: 94.9 nm

Comparative Dye

λmax: 562.6 nm (in ethyl acetate)
Half-value width: 88.1 nm

As the comparative dye there was used Comparative Dye a shown below:

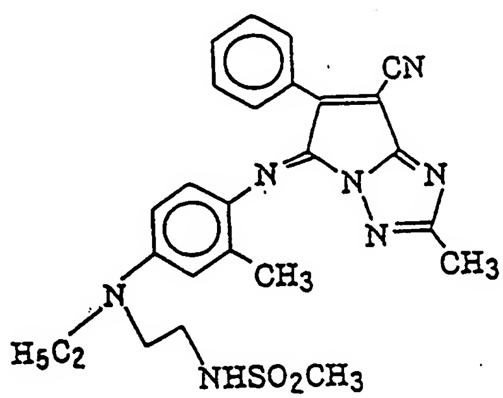


Fig. 1 shows that the dye of the present invention exhibits a sharp absorption, a reduced undesirable absorption in the yellow portion and a maximum absorption suitable as cyan dye.

On the other hand, it is shown that Comparative Dye a wherein the substituent R^7 in the coupler portion is a phenyl group (σ_p is smaller than 0.15) doesn't exhibit cyan color.

The maximum absorption wavelength (λmax) of other exemplary compounds of the present invention in ethyl acetate are set forth below:

Compound (I-22):	618 nm
Compound (I-4):	606 nm
Compound (I-7):	619 nm
Compound (I-10):	616 nm

REFERENTIAL EXAMPLE 1

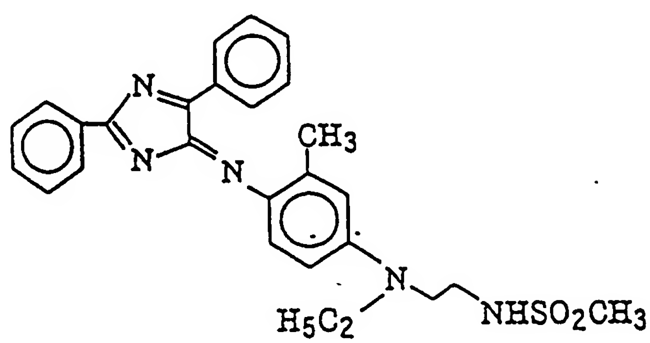
The dyes of the present invention were examined for fastness to light in a solution system. The dyes thus examined and the test results are set forth in Table 1.

Condition:	merry-go-round type xenon radiator (produced by Dojun Koki K.K.; output: 500 W, 100,000 lux)
Cell:	quartz cell
Solvent:	acetonitrile
Concentration:	3.0×10^{-5} (mol/ℓ)
Percent residue:	represented by the change (%) in the concentration at λmax from before to after forced discoloration test

Table 1

Dye	Irradiation Time	Ultraviolet Light Filter	Percent Residue	Remarks
I-2	60 min.	None	50	Invention
I-4	"	"	59	"
I-7	"	"	54	"
I-10	"	"	62	"
b	"	"	43	Comparison

Comparative Dye b:



REFERENTIAL EXAMPLE 2

In order to demonstrate the usefulness of the dyes of the present invention as filter dyes, the following model filters were prepared and examined for fastness to light.

Onto a 100-μm thick polyethylene terephthalate film (produced by Teijin Limited) which had been rendered heat resistant and smoothened on its back side as a support was coated a dye dispersion layer coating composition having the following formulations by a wire bar coating process to prepare a model filter. The thickness of the coating was adjusted such that the density after drying reached 2.0.

Dye dispersion layer coating composition:

Dye (I-1)	1.0 g
Polyvinyl butyral resin (Denka Butyral 5000-A produced by Denki Kagaku Kogyo K.K.)	3.0 g
Toluene	50 cc
Methyl ethyl ketone	50 cc
Polyisocyanate (Takenate D110N produced by Takeda Chemical Industries, Ltd.)	0.2 cc

Model filters were prepared in the same manner as above except that Dye (I-1) was replaced by other dyes set forth in Table 2.

The model filters thus prepared were irradiated with light from a 17,000 lux fluorescent lamp for 14 days to examine the stability of the dyes. For evaluation of the dye stability, the ratio of the density measured before to after irradiation was determined. The results are set forth in Table 2.

Table 2

Dye	Percent REsidue	Remarks
I-1	95	Invention
I-2	93	"
I-4	94	"
I-7	94	"
I-10	95	"
b	85	Comparison

The results set forth above show that the dyes of the present invention exhibit a remarkable fastness to light as compared with the comparative dyes.

REFERENTIAL EXAMPLE 3

Onto a commercially available uncoated base paper (basis weight: 64 g/m^2) was coated a coating solution consisting of 43 parts (by weight calculated in terms of solid content, hereinafter the same) of finely divided hollow grains of a styrene-acrylic ester copolymer (grain diameter: 0.3 to 0.4 μm), 17 parts of vapor phase process anhydrous silica (grain diameter: 12 nm), 12 parts of a styrene-butadiene copolymer latex, 18 parts of a polyvinyl acetate latex and 10 parts of finely divided grains of polymethyl methacrylate (grain diameter: about 8 μm) by means of a wire bar in such an amount that the solids content reached 10 g/m^2 to prepare a paper for ink jet recording.

Ink jet recording was made on this recording paper with Ink A having the following formulations. In this ink jet recording, an electrostatic acceleration type ink jet apparatus equipped with a head having a nozzle pore diameter of 50 μm and a dot density of 8/mm was used.

Ink A:

Dye (I-1) of the present invention	6 g
Diethyl phthalate	30 g
Diisopropyl adipate	44 g
N,N-Diethyldodecanamide	20 g

This ink exhibited an excellent dischargeability, and a sharp and high density cyan image was obtained.

Similar ink jet recording tests were effected except that Dye (I-1) was replaced by Dyes (I-7) and (I-10), respectively, in the same gram equivalent. As a result, all these dyes exhibited an excellent ink dischargeability and thus provided sharp and high density cyan images.

After these images were allowed to stand under indoor light for 3 months, the density thereof showed a drop of 1% or less.

REFERENTIAL EXAMPLE 4

(Preparation of heat transfer material)

The following materials were sufficiently dispersed in admixture to prepare a coating solution for smooth heat-resistant protective layer.

Formulations of coating solution:

Methyl methacrylate	10 g
n-Butyl acrylate	2 g
Benzoyl peroxide	0.1 g
Silica	35 g
Isopropyl alcohol (IPA)	15 g

The coating solution was diluted with a proper amount of a mixture of toluene and IPA. The coating solution was then coated on a 6-μm thick polyethylene terepthalate film (hereinafter referred to as "PET") as a substrate by means of a wire bar. The coated material was then dried at a temperature of 100°C for 1 minute to form a smooth heat-resistant protective layer with a thickness of about 1.5 μm.

A hot-melt ink having the following formulations was prepared.

Formulations of hot-melt ink:

Dye (I-1)	10 g
Barium salt of lanolin fatty acid	30 g
Carnauba wax	20 g
Paraffin wax	20 g
Dispersant	0.5 g
Liquid paraffin	5 g

The ink having the above mentioned formulations was then sufficiently dispersed with a mixture of 100 cc of methyl ethyl ketone and 130 cc of toluene at a temperature of 68°C by a ball mill for about 48 hours.

To the ink dispersion was added 300 g of a 20 wt.% vinyl chloride-vinyl acetate copolymer resin solution (10 parts of resin, 20 parts of toluene, 20 parts of methyl ethyl ketone). The mixture was then dispersed by a ball mill for about 1 hour to prepare a coating solution of heat-sensitive transfer composition.

This coating solution was coated on the surface of the above mentioned PET film opposite the smooth heat-resistant protective layer by means of a wire bar, and then dried at a temperature of 100°C for 1 minute to form a hot-melt ink layer having a thickness of about 5 μm.

The heat transfer material thus obtained was laminated with a plain paper as a heat transfer image-receiving material in such an arrangement that the transfer layer (hot-melt ink layer) in the heat transfer material was brought into contact with the plain paper. Printing was effected by a heat head on the heat transfer material from the support side to cause transfer. As a result, a sharp cyan color recording was provided.

Heat transfer materials were prepared in the same manner as above except that Dye (I-1) was replaced by Dyes (I-7) and (I-10), respectively, in the same gram equivalent weight. Using these heat transfer materials, transfer was similarly effected. As a result, a sharp cyan color recording was provided.

These recorded sheets were then examined for stability of image to light. A high image stability to light was obtained.

The derivatives represented by formula (III) of the present invention are useful as synthesis intermediates of physiologically active substances such as pharmaceutical preparations and pesticides. These derivatives are also useful as couplers in the field of photographic chemistry.

On the other hand, the compounds represented by formulae (I) and (II) are useful dyes which are advantageous in that they exhibit a reduced secondary absorption and a primary absorption wavelength of 600 nm or more.

When used as an image forming dye in ink jet recording process, heat-sensitive transfer recording process, etc., the novel pyrrolotriazole azomethine dye of the present invention provides a high density image free of discoloration because of its remarkably excellent fastness to light.

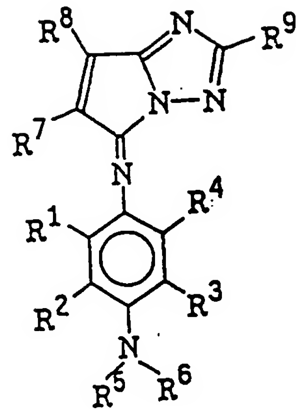
Also, when used as various filter dyes, the azomethine dye of the present invention provides a filter with an excellent stability and a remarkably reduced density drop because of its excellent fastness to light.

Furthermore, when image formation is effected on a heat transfer dye providing material comprising the pyrrolotriazole azomethine dye of the present invention, it provides an image with a high fastness to heat and light and an excellent color reproducibility.

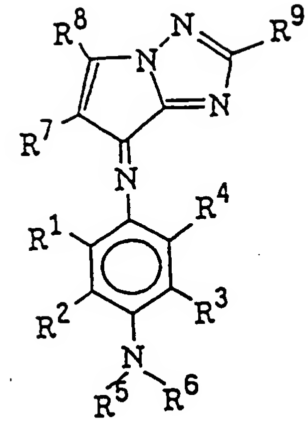
Moreover, the pyrrolotriazole azomethine dye of the present invention provides the heat transfer dye providing material with a better storage stability when used in admixture with one or more present azomethine dyes than when used singly.

Claims

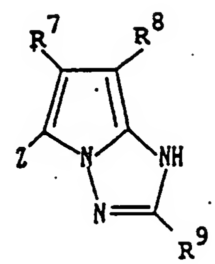
1. A pyrrolotriazole derivative represented by any one of formulae (I), (II), or (III):



(I)



(II)



(III)

wherein:

R^1, R^2, R^3 and R^4 each independently represents a hydrogen atom or a nonmetallic atomic group;

R^5 and R^6 each independently represents a hydrogen atom, alkyl group, an aryl group, or a heterocyclic group;

R^7 represents an electrophilic group having a Hammett's substituent constant σ_p of 0.15 or more;

R^8 and R^9 each independently represents a hydrogen atom or a nonmetallic atomic group;

the sum of Hammett's substituent constant σ_p of R^7 and R^8 is 0.65 or more;

R^1 and R^2, and/or R^2 and R^5, and/or R^5 and R^6, and/or R^6 and R^3, and/or R^3 and R^4 may be connected to each other to form a cyclic structure;

R^7 and R^8 may be connected to each other to form a cyclic structure; and

Z represents a hydrogen atom, a halogen atom, an arylthio group, a heterocyclic thio group, an arylsulfinyl group, or a nitroso group.

2. A pyrrolotriazole derivative as in claim 1, wherein said pyrrolotriazole derivative is a pyrrolotriazole azomethine dye represented by any one of formulae (I) or (II).

3. A pyrrolotriazole derivative as in claim 1, wherein said pyrrolotriazole derivative is a 1H-pyrrolo-[1,2-b]-[1,2,4]triazole derivative represented by formula (III).

4. A pyrrolotriazole derivative as in claim 1, wherein R^1, R^2, R^3 and R^4 each independently represents a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a heterocyclic group, a cyano group, a hydroxyl group, a nitro group, a carboxyl group, a sulfonic acid group, an amino group, an alkoxy group, an aryloxy group, an acylamino group, an aminocarbonylamino group, a sulfamoylamino group, an alkylthio group, an arylthio group, an alkoxycarbonylamino group, a sulfonylamino group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, an alkoxycarbonyl group, a heterocyclic oxy group, an azo group, an acyloxy group, a carbamoyloxy group, a silyloxy group, an aryloxycarbonyl group, an imido group, a heterocyclic thio group, a sulfinyl group, a phosphoryl group, a formyl group, an acyl group, or an azolyl group.

5. A pyrrolotriazole derivative as in claim 4, wherein R^2, R^3 and R^4 each represents a hydrogen atom; and R^1 represents a hydrogen atom, an alkyl group, or an acylamino group.

6. A pyrrolotriazole derivative as in claim 1, wherein said electrophilic group having a Hammett's substituent constant σ_p of 0.15 or more for R^7 is a formyl group, an acyl group, an acyloxy group, a carbamoyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a cyano group, a carboxyl group, a nitro group, a dialkylphosphono group, a diarylphosphono group, a diarylphosphinyl group, an alkylsulfinyl group, an arylsulfinyl group, an alkylsulfonyl group, an arylsulfonyl group, an arylthio group, a sulfonyloxy group, an acylthio group, a sulfamoyl group, an isocyanato group, a thiocyanato group, a thiocarbonyl group, an alkyl group substituted by at least two halogen atoms, an alkoxy group substituted by at least two halogen atoms, an aryloxy group substituted by at least two halogen atoms, an alkylamino group substituted by at least two halogen atoms, an alkylthio group substituted by at least two halogen atoms, an aryl group substituted by other electrophilic groups having a Hammett's substituent constant σ_p of 0.15 or more, a heterocyclic group, a chlorine atom, a bromine atom, or a selenocyanato group.

7. A pyrrolotriazole derivative as in claim 6, wherein said electrophilic group having a Hammett's substituent constant σ_p of 0.15 or more for R^7 is a cyano group or a -COR group, wherein R represents a hydrogen atom, an amino group, an alkoxy group, or an aryloxy group.

8. A pyrrolotriazole derivative as in claim 1, wherein R^8 represents a hydrogen atom, an aryl group, a heterocyclic group, an alkyl group, a cyano group, a carboxyl group, a formyl group, an acyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, an acylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a sulfonylamino group, an aminocarbonylamino group, a sulfamoylamino group, an amino group, an alkoxy group, an aryloxy group, a silyloxy group, a heteryloxy group, an alkylthio group, an arylthio group, a heterylthio group, a halogen atom, a hydroxyl group, a nitro group, a sulfamoyl group, a sulfonyl group, an azo group, an acyloxy group, a carbamoyloxy group, an imido group, a sulfinyl group, a phosphoryl group, or an azolyl group, provided that the sum of Hammett's substituent constant σ_p of R^7 and R^8 is 0.65 or more.

9. A pyrrolotriazole derivative as in claim 8, wherein R^8 represents a cyano group or -COR, wherein R represents a hydrogen atom, an amino group, an alkoxy group, or an aryloxy group.

10. A pyrrolotriazole derivative as in claim 1, wherein R^9 represents a hydrogen atom, an aryl group, a heterocyclic group, an alkyl group, a cyano group, a carboxyl group, a formyl group, an acyl group, a carbamoyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, an acylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a sulfonylamino group, an aminocarbonylamino group, a sulfamoylamino group, an amino group, an alkoxy group, an aryloxy group, a silyloxy group, a heteryloxy group, an alkylthio group, an arylthio group, a heterylthio group, a halogen atom, a hydroxyl group, a nitro group, a sulfamoyl group, a sulfonyl group, an azo group, an acyloxy group, a carbamoyloxy group, an imido group, a sulfinyl group, a phosphoryl group, or an azolyl group.

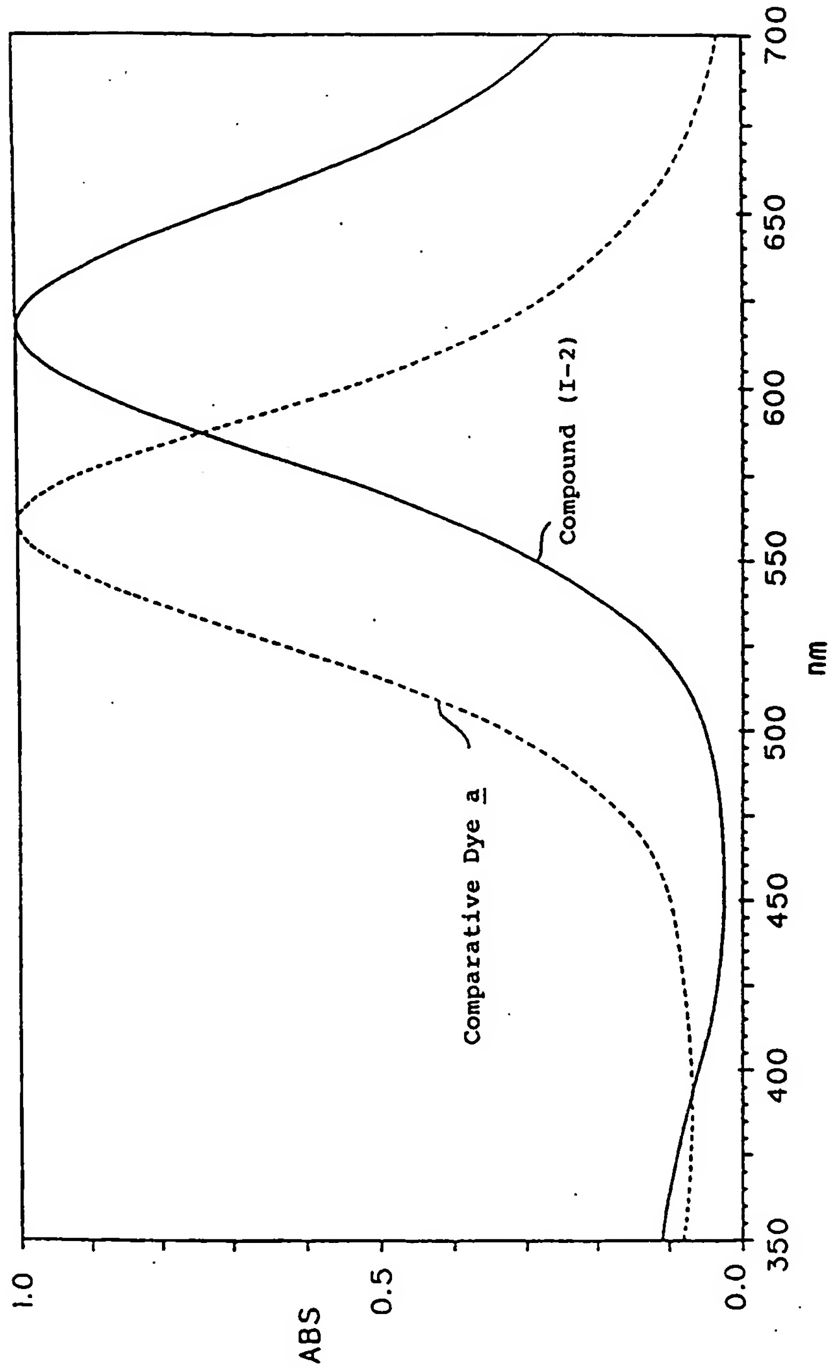
11. A pyrrolotriazole derivative as in claim 10, wherein R^9 represents an aryl group.

12. A pyrrolotriazole derivative as in claim 11, wherein R^9 represents an unsubstituted aryl group or an aryl group substituted by at least one of substituents selected from a nitro group, a halogen atom, a cyano group, an acylamino group, and a sulfonamido group.

13. A pyrrolotriazole derivative as in claim 3, wherein R^7 and R^8 each independently represents a cyano group or a -COR group, wherein R represents a hydrogen atom, an amino group, an alkoxy group, or an aryloxy group; and R^9 represents an aryl group.

14. A pyrrolotriazole derivative as in claim 13, wherein Z represents a hydrogen atom; a halogen atom; an unsubstituted arylthio group; an arylthio group substituted by at least one of substituents selected from a halogen atom, an alkyl group, an alkoxy group, a cyano group, an aryloxycarbonyl group, an alkoxycarbonyl group, a ureido group, an alkoxycarbonylamino group, an acylamino group, and a carboxyl group; an unsubstituted arylsulfinyl group; or an arylsulfinyl group substituted by at least one of substituents selected from a halogen atom, an alkyl group, an alkoxy group, a cyano group, an alkoxycarbonyl group, and a carboxyl group.

FIG. 1


ABS
1.0
0.5
0.0
350
400
450
500
550
600
650
700
nm
Comparative Dye a
Compound (I-2)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 10 9588

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 252 288 (KONISHIROKU SHASHIN KOGYO K.K.) * page 6, line 16 - page 7, line 25; claims 1,2 * * page 14; examples A-3 * * page 16; examples C-3 * * page 17, line 52 - line 55 *	1-14	C07D487/04
X	PATENT ABSTRACTS OF JAPAN vol. 12, no. 180 (P-709)10 June 1986 & JP-A-62 289 837 (KONISHIROKU SHASHIN KOGYO K.K.) 16 December 1987	1,3,8-10	
A	* abstract *	2,4-7, 11-14	
A	US-A-4 093 728 (P.C.WADE ET AL.) * column 1, line 1 - line 27; claim 1 *	1-14	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C07D
B41M
C09B
G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 JULY 1992	BACON A.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)